A Nonmetal Interaction Model for the Segregation of Trace Metals during Solidification of Fe-Ni-S, Fe-Ni-P, and Fe-Ni-S-P Alloys

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As nonmetals are added to the Fe-Ni system, segregation coefficients (k) of trace constituents change dramatically. For example, as the S content of the metallic liquid increases from 0 to ~31 wt pct, the molar k(Ge) between solid and liquid metal increases from 0.6 to ~120. Little of this change can be ascribed to temperature. Also, these changes are not linear. In the case of the Fe-Ni-S system, the largest changes are seen between 20 and 30 wt pct S. Here we present a model for the interaction of nonmetals with other species in metallic systems. The model assumes that the nonmetal either repels or attracts tracers (E) in the metallic liquid, causing those tracers to either segregate strongly into the solid metal or to have enhanced solubility in the liquid. Examples of both types of behavior are given. The model predicts that the activity coefficient of the tracer (γ_E) should correlate linearly with $(1 - \alpha n X_N)$, where X_N is the mole fraction of the nonmetal in the metallic liquid, n is a stoichiometry factor related to the speciation of N in the liquid, and α is a constant. Indeed, good linear correlations of $\ln(k)$ vs $\ln(1 - \alpha n X_N)$ are found for all elements where there is a measurable effect. Thus, if the composition of the metallic liquid is known, a segregation coefficient of a trace constituent may be predicted—even if the temperature, exact Fe/Ni ratio, and information about the activity coefficient in the solid phase are unknown. The nonmetal interaction model presented here can be related to more traditional methods of modeling activity coefficients (i.e., power law expansions) and can be shown to be a special case of this type of parameterization. Comparison of model predictions of first-order (sulfur-E) interaction coefficients (ε) to measured values yields acceptable agreement for some elements, such as P and Ge, and all elements except Ni agree to within a factor of 3. The predictive model described above, based on equilibrium experiments, may be used to evaluate the segregation coefficients extracted from the dynamic ("plane front solidification") experiments of Sellamuthu and Goldstein.[10,11] Contrary to claims, reliable segregation coefficients are not extractable from dynamic experiments.

(1-aX)- This is equivalent to effective metal ions present in the melt.

I. INTRODUCTION

AN understanding of the effects of nonmetals in metallic systems is of importance in metallurgy. Additionally, in the field of planetary science, such knowledge is especially important, because the interactions between metals and nonmetals likely played important roles during the formation of iron meteorites and during core formation in the terrestrial planets.

We present here an internally consistent model for understanding changes in trace element (metallic solid/metallic liquid) segregation coefficients (k) as a function of changes in nonmetal concentrations in the metallic liquid. This model can be related to more traditional metallurgical measurements of interaction coefficients in metallic liquids. The nonmetal-interaction model for the Fe-Ni-S and Fe-Ni-P systems can be modified to predict partitioning behavior in the more complex Fe-Ni-S-P system. We tentatively take these successes as a posteriori confirmation that the many simplifying assumptions of our model are justified. Our model can account for the partitioning behavior of several elements—Co, Cr, Au, Ge, Ga, Ir, Ni, and P—with distinctly different chemical behaviors in metallic systems.

II. THE MODEL

A. Thermodynamics of Segregation

Consider the equilibrium solid/liquid segregation of an element. At equilibrium, the chemical potential of element E is the same in both phases:

$$\mu_E^{Solid} = \mu_E^{Liquid} \qquad [1]$$

These chemical potentials can be expressed in terms of a standard state chemical potential and an activity:

$$\mu_E^{Solid,0} + RT \ln(a_E^{Solid}) = \mu_E^{Liquid,0} + RT \ln(a_E^{Liquid}) \qquad [2]$$

where R is the gas constant and T is temperature in Kelvin. Rearranging Eq. [2] gives

$$\ln(a_E^{Solid}/a_E^{Liquid}) = (\mu_E^{Liquid,0} - \mu_E^{Solid,0})/RT \qquad [3]$$

The activity can be expressed as

$$a = \gamma X_E \qquad [4]$$

where γ is the activity coefficient and X is the mole fraction of E. Expanding Eq. [3] using Eq. [4] gives

$$\ln(X_E^{Solid}/X_E^{Liquid})$$
$$= -\ln(\gamma_E^{Solid}/\gamma_E^{Liquid}) + (\mu_E^{Liquid,0} - \mu_E^{Solid,0})/RT \qquad [5]$$

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The left-hand side of Eq. [5] is the natural logarithm of the molar segregation coefficient (k). Equation [5] can be simplified further under certain assumptions.

B. *The Effect of Temperature*

We assume that the k values which we and others measure in the Fe-Ni-S-P system[1,2,3] are very weak functions of temperature and are instead strong functions of the composition of the metallic liquid. The justification for this approach is empirical. Measured k values are more easily parameterized in terms of composition than in terms of temperature. For example, the value of k(Ge) increases from 0.6 to ~120 in the Fe-Ni-S system[3] as the concentration of S in the metallic liquid increases from 0 to ~31 wt pct (Figure 2). This change cannot be ascribed simply to temperature (*i.e.*, to ideal changes in k), because heats of fusion in metallic systems are small. In an ideal system, changes in $\ln k$ vary only with temperature and change as $\Delta H_{fusion}/(RT^2)$. Typical heats of fusion of pure metals are ~1 to 5 kcal/mole, which are only large enough to change k by (at most) a factor of 2 as temperature changes from 1500 °C to 1000 °C. Also, by changing the Fe/Ni ratio of an experimental system, it is possible to maintain equilibrium between solid and liquid metals at different temperatures without changing the nonmetal content of the metallic liquid. Comparison of two such experiments showed no measurable change in the segregation coefficient—even after a temperature change of 50 K.[1,3] Thus, we conclude that segregation coefficients in Fe-Ni metallic systems are very weak functions of temperature (and Fe/Ni ratio) and that the concentration of nonmetals in the system is of primary importance. In past efforts, both we and others have assumed that k values in the Fe-Ni-S and Fe-Ni-P systems were best parameterized in terms of composition—not temperature.[1,3]

C. *The Effect of γ_E^{Solid}*

We also assume that, relative to the changes in γ_E^{Liquid}, changes in γ_E^{Solid} are small. We rationalize this assumption based on the following observations. (1) Segregation coefficients for most tracers between solid and liquid Fe-Ni metal in the nonmetal-free system are usually about unity within a factor of 2. This implies that, relative to the liquid, solid Fe-Ni is not particularly nonideal, with the segregating element showing little preference for either solid or liquid. This observation is reinforced by the complete miscibility of Fe-Ni alloys at high temperature and by the narrowness of the solidus-liquidus loop of the Fe-Ni system. (2) One exception to observation (1) is k(P). In the S-free system, k(P) is ~0.1, and therefore, relative to the liquid, the solid solution must be very nonideal. However, in the Fe-Ni-P system, the changes in k(P) between high-temperature dilute solutions of P and low-temperature eutectic compositions are small (≤30 pct; Table I). This, in turn, implies that $\gamma_P^{Solid}/\gamma_P^{Liquid}$ is effectively constant in the metal-saturated portion of the Fe-Ni-P system. (3) The segregation coefficient of Ni in the Fe-Ni-P system remains essentially constant from the liquidus of the P-free system to the eutectic temperature (Table I). From this, we infer (a) that the interaction of Ni and P is weak (weaker even than

the Ni-S interaction) and (b) that the effect of temperature on k(Ni) is small. If (a) and (b) are not true, then the ideal and nonideal influences on k(Ni) must effectively cancel over a wide range of temperature. Again, we postulate that metal-nonmetal and S-P interactions in the liquid are much stronger than nonidealities in the solid, and we will return to this point in the next section.

D. *Modeling Segregation Coefficients*

Thus, in the absence of strong metal-nonmetal or nonmetal-nonmetal interactions in the liquid, there is apparently no strong driving force for k(E) to change with temperature or changing liquid composition. To the extent that this approximation is true, Eq. [5] can be rewritten as a function of γ_E^{Liquid} only; *i.e.*,

$$\ln k(E) = -\ln (1/\gamma_E^{Liquid}) + C = \ln (\gamma_E^{Liquid}) + C \quad [6]$$

relating the segregation coefficient to the activity coefficient in the liquid phase. In this form, the constant C should be the value of $\ln k$(E) in the nonmetal-free system and contains such terms as the solid and liquid activity coefficients in the nonmetal-free system.

Work on the thermodynamics of dilute liquid iron alloys[4] has shown that free energy interaction coefficients can be used to expand the activity coefficient about the infinitely dilute reference state, giving

$$\ln \gamma_i = \ln \gamma_i^0 + \sum_{j=2}^{n} \varepsilon_i^j X_j + \sum_{j=2} \rho_i^j X_j^2 + \cdots \quad [7]$$

where ε_i^j is the first-order interaction coefficient and ρ_i^j is the second-order interaction coefficient. If we consider the example of the partitioning of Ge in the Fe-Ni-S system and neglect terms higher than first order, we obtain the expanded form

$$\ln \gamma_{Ge} = \ln \gamma_{Ge}^0 + (\varepsilon_{Ge}^{Ge} X_{Ge} + \varepsilon_{Ge}^{Ni} X_{Ni} + \varepsilon_{Ge}^{S} X_S) \quad [8]$$

Given this formalism, one should be able to express segregation coefficients simply in terms of a linear combination of the mole fractions of the melt component species weighted by their respective interaction coefficients. A difficulty with this approach is that interaction coefficients are often unknown, or poorly known, and require higher order terms as solute concentrations become less dilute. These interaction coefficients may also be functions of temperature or other intensive variables.

Below we will show that good fits to the experimental segregation data are obtained when the activity coefficient is simply expressed as

$$\ln \gamma = \beta \ln (1 - \alpha n X_N) \quad [9]$$

or in terms of the segregation coefficient

$$\ln k(E) = \beta \ln (1 - \alpha n X_N) + C \quad [10]$$

where α is a constant that is specific to the system, β is a constant that is a measure of the interaction between the tracer element and the nonmetal species, n is a stoichiometry factor related to the speciation of the nonmetal in the metallic liquid, and X_N is the mole fraction of the nonmetal species in the liquid. In the Fe-Ni-S system, the nonmetal species is taken to be FeS.[5] The choice of

Table I. Experiments, Segregation Coefficients, and Composition of the Metallic Liquid*

Fe-Ni System

Reference	Experiment	Tracers	k(Tr. 1)	k(Tr. 2)	k(Ni)
8	28 XI 77			—	0.83
8	7 XII 77	Cr	0.53	—	0.89
8	11 II 78	Au	0.17	—	0.84
8	16 II 78	Co	0.97	—	0.90
1	6	Au	0.75	—	1.06
1	7	Cu	1.05	—	1.07
1	8	Cr	0.64	—	1.11
Misc. UA	—	W, Ga	0.86	0.91	0.84
Misc. UA	—	Ir	1.43	—	0.91
Misc. UA	—	Au	0.39	—	0.90
Misc. UA	—	Au	0.45	—	0.89

Fe-Ni-S System

Reference	Experiment	Tracers	k(Tr. 1)	k(Tr. 2)	k(Ni)	liq X_S
1	19	Ge	1.41	—	0.99	0.147
1	18	Ge	9.43	—	1.66	0.382
1	21	Ir	4.29	—	0.99	0.134
1	20	Ir	12.84	—	1.46	0.360
1	17	—	—	—	0.97	0.069
3	12g	Ge	0.74	—	0.92	0.035
3	12e	Ge	0.72	—	0.94	0.042
3	13f	Ge	0.70	—	0.92	0.048
3	12c	Ge	0.76	—	0.94	0.063
3	12a	Ge	0.76	—	0.97	0.096
3	12b	Ge, Au	1.20	0.42	1.06	0.166
3	13d	Ge	1.48	—	1.06	0.209
3	12f	Ge	1.77	—	1.11	0.223
3	12h	Ge	1.91	—	1.16	0.237
3	13c	Ge	6.80	—	1.52	0.334
3	13a	Ge	8.15	—	1.54	0.350
3	16f	Ge, Ga	8.36	5.88	1.59	0.356
3	13e	Ge	8.75	—	1.76	0.365
3	16e	Ge, Ga	10.83	11.71	1.66	0.378
3	13h	Ge	15.97	—	1.58	0.386
3	Jam-1	Ge, Cr	120.00	0.10		0.440
3	14b	Ir, Au	9.06	0.46	1.09	0.202
3	14a	Ir, Au	7.19	0.46	1.12	0.206
3	19d	Ir, Au	49.00	1.12	1.47	0.343
3	14d	Ir, Au	56.00	1.30	1.52	0.347
3	14c	Ir, Au	101.00	1.15	1.55	0.356
3	18c	Ir, Ga	6.94	1.61	1.12	0.188
3	18d	Ir, Pb	7.07	—	1.12	0.204
3	17	Au, Pb	1.03	0.01	1.48	0.320
3	21d	W	2.79	—	1.10	0.164
3	21c	W	3.01	—	1.05	0.172
3	21g	W	24.00	—	1.43	0.289
3	21h	W	32.00	—	1.66	0.358
Misc. UA	22e	Au	0.52	—	1.17	0.226
Misc. UA	23a	Ir	3.50	—	0.96	0.108
Misc. UA	22h	Cr	0.17	—	1.56	0.399
Misc. UA	52	Co	2.85	—	1.51	0.362
Misc. UA	56a	Co	2.58	—	1.54	0.352
Misc. UA	56b	Co	2.77	—	1.60	0.367
Misc. UA	6A.1	Ir	29.00	—	1.25	0.305
Houston	10	Ge	125.00	—	2.38	0.440
Houston	11	Au	4.50	—	2.35	0.429
Houston	14	Au	8.00	—	2.40	0.431
Houston	15	Ge	211.00	—	2.36	0.435

Fe-Ni-P System

Reference	Experiment	Tracers	k(Tr. 1)	k(Ni)	k(P)	liq X_P
9	E11	Ge	1.71	0.89	0.12	0.151
9	E5**	Ge	1.46	—	0.13	0.113
9	E4**	Ge	1.29	—	0.10	0.107

Table I. Cont. Experiments, Segregation Coefficients, and Composition of the Metallic Liquid*

Fe-Ni-P System

Reference	Experiment	Tracers	k(Tr. 1)	k(Ni)	k(P)	liq X_P
9	E10**	Ge	1.00	—	0.09	0.083
9	E8**	Ge	0.73	—	0.07	0.051
1	12a	Ga	1.05	0.92	0.10	0.059
1	12b	Ga	1.22	0.93	0.12	0.078
1	13a	Au	0.57	0.91	0.12	0.099
1	13b	Au	0.78	0.94	0.13	0.134
1	15	Ir	2.28	0.89	0.10	0.059
1	14	Ir	2.87	0.90	0.12	0.091
7	23c	Ir	4.94	0.95	0.11	0.113
7	23e	Ge	1.38	0.89	0.12	0.113
7	23g	Au	0.68	0.90	0.12	0.106
7	23b	Ir	2.91	0.92	0.09	0.078
7	23d	Ge	1.05	0.91	0.09	0.074
7	23f	Au	0.61	0.93	0.11	0.077
Houston	22†	Au	0.53	0.39	0.24	0.134
Houston	23†	Ge	2.23	0.26	0.19	0.137
Houston	24‡	Ir	5.4/BDL	0.91/0.42	0.12/0.23	0.137
Houston	25	Ge	2.30	0.95	0.11	0.146
Houston	26	Au	0.99	0.93	0.12	0.143

*The literature data have been converted to mole fractions. The references to "Misc. UA" are for unpublished data from the University of Arizona. References to Houston are for unpublished data from NASA/JSC.
**Nickel was not reported in the reference; a nominal Ni value of 10 pct is assumed for the purposes of calculating molar k values.
†These experiments contain only alpha-iron as the solid phase.
‡This experiment contains both the alpha- and gamma-iron phases; multiple values in columns are for gamma/alpha, respectively. "BDL" indicates below detection limit.

speciation for the Fe-N-P system is not as straightforward as the Fe-Ni-S system. Reasonable choices for the speciation of P are Fe_3P and Fe_2P. Here we have used Fe_3P but recognize that this may not be optimal. Thus, because we have assumed the metallic liquid speciations of S and P to be FeS and Fe_3P, respectively, activity coefficients will be proportional to $(1 - 2\alpha X_S)$ in the Fe-Ni-S system and to $(1 - 4\alpha X_P)$ in the Fe-Ni-P system. In the S-bearing system, the S not only takes up a volume element of the liquid but combines with an Fe so that the total number of sites available to elements that avoid sulfur is reduced by two. In the P-bearing system, the number of sites is correspondingly reduced by four. This formalism ignores the effects of metallic elements (such as Ni) in the liquid on the activity of the trace element. In effect, we have assumed that the liquid contains "domains" that either accept siderophile tracers, such as Ge, Ir and Au (which are doped at the ~1 wt pct level), or exclusively reject them. The concept of domains is, in fact, the basis for the derivation of Eq. [9]. The domains which exclude the metallic elements are defined to be nonmetal-rich. Conversely, these nonmetal domains may attract tracers such as Cr or Ag, which are chalcophile and readily associate with S in the metallic liquid. Thus, as nonmetal concentrations of metallic liquids increase, segregation coefficients may either increase or decrease, depending on the chemical affinity of the partitioned element for nonmetals. In this model, the volume of the domain is related to the strength of the tracer-nonmetal interaction, β.

We note further that the series expansion of a simplification of Eq. [9] gives

$$\ln(1 - X_N) = -X_N - (X_N)^2/2$$
$$- (X_N)^3/3 - (X_N)^4/4 - \dots \quad [11]$$

Thus, within our Eq. [9], we have all the nonconstant terms of the more traditional Eq. [7] but ignore all interaction coefficients except the ones between the nonmetal and the tracer (e.g., Ge and S in Eq. [8]). Even so, Eq. [9] is not as general as Eq. [7], in that the higher order interaction coefficients cannot be independent of ε_E^N. For example, ρ_E^N would be constrained to equal $(0.5 * \varepsilon_E^N)$ in expansions such as Eq. [11].

III. RESULTS

Tables I and II list the experimental data which we have used in the regressions of segregation coefficients vs the nonmetal contents of the metallic liquid. Most of the experiments have been performed by us either at the University of Arizona or at NASA Johnson Space Center, although some data from the Lehigh University (Bethlehem, PA) group of J.I. Goldstein have been used as well. In general, the experiments represent isothermal equilibrium of solid and liquid metal and are analyzed using established electron microbeam techniques.[3] Most of the data in Table I has already been published elsewhere.[1,2,3,7,8,9] Because of the modest Ni contents in these experimental systems (~10 wt pct), the solid phase should be γ-iron. However, in some of the low-temperature experiments, when the concentration of the tracer in the solid becomes appreciable, we cannot positively rule out that there is occasional stabilization of the α-iron phase. However, the only definite appearance of the α phase was in three low-temperature experiments in the Fe-Ni-P system (Table I; Houston 22, 23, and 24). In one experiment (Houston 24), both α- and γ-iron are present. The data have been converted to mole fractions, and the segregation coefficients are the ratios of the mole

Table II. Summary of Experiments in the Fe-Ni-S-P System*

Fe-Ni-S-P System

Reference	Experiment	Tracers	k(Tr.)	k(Ni)	k(P)	liq X_P	liq X_S
3	21b	P	—	0.99	0.12	0.030	0.072
3	21a	P	—	1.03	0.13	0.032	0.138
3	21f	P	—	1.35	0.31	0.018	0.282
3	21e	P	—	1.57	0.77	0.006	0.329
7	40a	Ge	4.92	1.42	0.51	0.007	0.318
7	40b	Ge	1.88	1.09	0.15	0.035	0.177
7	40c	Ge	1.41	0.99	0.11	0.077	0.075
7	40d	Ge	1.32	0.99	0.13	0.082	0.045
7	41b	Ge	3.15	1.16	0.17	0.035	0.196
7	43a	Ge	2.02	1.07	0.16	0.035	0.177
7	43b	Ge	2.86	1.15	0.20	0.031	0.196
7	43c	Ge	2.60	1.08	0.18	0.031	0.193
7	43d	Ge	2.39	1.08	0.21	0.028	0.199
7	43e	Ge	2.33	1.10	0.18	0.033	0.190
7	43g	Ge	2.32	1.17	0.21	0.028	0.212
7	47a	Ge	2.30	1.12	0.21	0.033	0.203
7	47b	Ge	2.75	1.25	0.26	0.024	0.245
7	47c	Ge	2.38	1.07	0.20	0.033	0.172
7	48b	Ge	0.89	0.98	0.12	0.011	0.103
7	50a	Ge	1.16	0.95	0.12	0.076	0.023
7	50b	Ge	1.15	0.92	0.10	0.080	0.018
7	55b	Ge	3.82	1.26	0.31	0.019	0.273
7	55a2	Ge	3.43	1.20	0.27	0.017	0.272
7	55a1	Ge	1.97	1.08	0.20	0.026	0.185
7	57a	—	—	1.84	2.02	0.002	0.414
7	57c	—	—	1.84	1.89	0.002	0.394
7	59a	—	—	1.20	0.20	0.009	0.242
7	59b	Au	0.44	1.09	0.16	0.007	0.192
7	59c	Ge	1.73	1.05	0.15	0.007	0.215
Misc. UA	4B	Cr	0.48	1.06	0.17	0.037	0.192
Misc. UA	4C	W	3.42	1.12	0.20	0.034	0.198
Misc. UA	5	—	—	1.06	0.12	0.030	0.055
Houston	13	—	—	2.03	3.76	0.004	0.433
Houston	16	—	—	2.29	3.78	0.005	0.414

*The literature data have been converted to mole fractions. References as in Table I.

fraction in the solid metal to the mole fraction in the metallic liquid.

Linear regressions of ln (k) vs ln $(1 - 2\alpha X_S)$ were made for the experiments in the Fe-Ni-S system and similarly, regressions of ln (k) vs ln $(1 - 4\alpha X_P)$ were performed for experiments in the Fe-Ni-P system. An optimal value of $\alpha = 1.09$ was obtained by trial and error for the Fe-Ni-S system; α for the Fe-Ni-P system was taken to be 1.36. These values are close to the values needed to make the activity of FeS and Fe$_3$P unity at the eutectics of the Fe-S and Fe-P systems. For example, the activity of FeS at the eutectic must be unity even though the mole fraction of FeS is only 0.88. For ln $(1 - 2\alpha X_S)$ to approach minus infinity at the eutectic requires that $\alpha = 1.14$.

The model results for tracers in the Fe-Ni-S system (for which we have the most data) are shown in Figures 1 through 8, and the slope and intercept for each regression are summarized in Table III. The slopes (β) are measures of the extent of the nonmetal interaction with the tracer element. The intercepts are very close to the values of ln (k) in nonmetal-free systems. With the exception of the ln k(Ni) vs ln $(1 - 4\alpha X_P)$ regression, the correlation coefficients for the regressions are all greater than 0.9. [This one exception occurs because P is not

known to influence k(Ni).] In general, the regressions fit the experimental data to within 10 to 20 pct, the typical experimental error.

Thus, given a nonmetal concentration in either the Fe-Ni-S or Fe-Ni-P system, it is very straightforward to predict a segregation coefficient by using our regressions. No knowledge of the temperature, the exact Fe/Ni ratio, or the solid-phase activity coefficients is required. Also, even though our model was devised to describe only metal-nonmetal interactions, it appears that changes in k(P) as a result of interaction with S may also be predicted using our formalism.

A. Influence of T and γ^{Solid}

We now return to the assumptions that we made earlier concerning the relative importances of temperature and nonidealities in the solid solution. First, the model fits the data very well even though terms for these other intensive variables have not been considered. Consequently, if temperature and/or γ_E^{Solid} are important, then either the overall effects of temperature and nonidealities in the solid and liquid must combine to yield the functional form that we have given or all of these terms (i.e., T, γ_E^{Solid}, and γ_E^{Liquid}) must have the same functional form. Considering that we have only used liquid mole fractions

k(Ni) in the Fe-Ni-S system
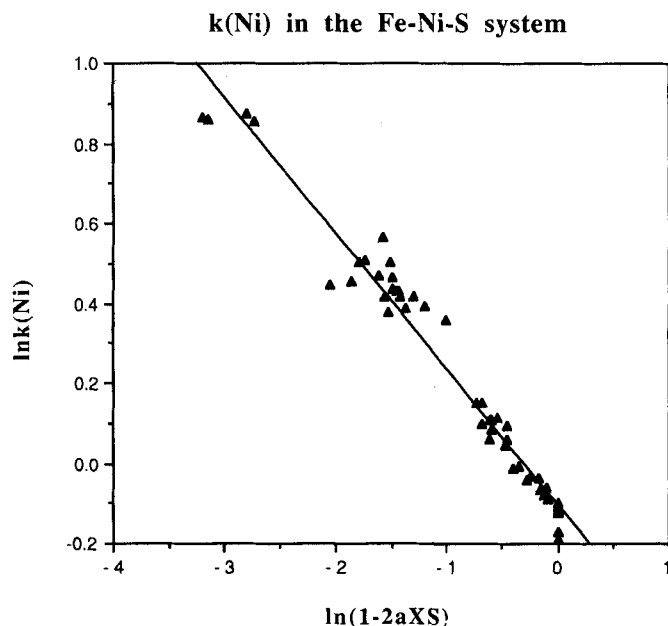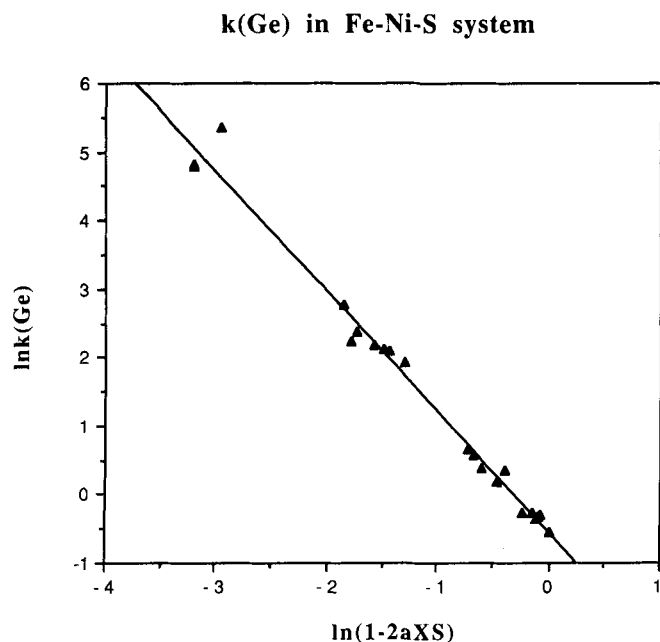

Fig. 1—Ln k(Ni) vs ln $(1 - 2\alpha X_S)$. The natural logarithm of the molar Ni segregation coefficient (D) is linearly related to ln $(1 - 2\alpha X_S)$ in the metallic liquid, where $\alpha = 1.09$. There is a good linear relationship that holds over a range of D(Ni) of approximately a factor of 2. This range of D(Ni) corresponds to a temperature range of 450 °C and 0 to 31 pct S in the metallic liquid. The experimental data are given in Table I, and the parameters of the regression are also listed in Table II.

k(Ge) in Fe-Ni-S system

Fig. 2—Ln k(Ge) vs ln $(1 - 2\alpha X_S)$. The natural logarithm of the molar Ge segregation coefficient is linearly related to ln $(1 - 2\alpha X_S)$ in the metallic liquid—again, $\alpha = 1.09$. The two high ln k(Ge) data have larger than normal uncertainties but agree extremely well with each other. Here the linearity holds over a range of k(Ge) that spans a factor of 200X. The temperature range and range of pct S is the same as in Fig. 1. The experimental data are given in Table I, and the parameters of the regression are also listed in Table II.

k(Ir) in Fe-Ni-S System

Fig. 3—Ln k(Ir) vs ln $(1 - 2\alpha X_S)$. Same as Figs. 1 and 2 but for Ir. As in the case of Ge, the range of k values spans a factor of ~100. One experiment from Ref. 1 in Table I, which appears not to have approached equilibrium, was omitted from the figure and the regression.

to construct our model, we consider either of these alternatives as unlikely. We do not dispute that terms other than γ_E^{Liquid} affect k(E), but we do question whether these effects are important. Second, the success of the model for both "compatible" and "incompatible" elements is impressive, even though the roles of γ_E^{Solid} for elements whose k(E) > 1 ("compatible"; e.g., Ir) and elements whose k(E) < 1 ("incompatible"; e.g., Au) may be very different (e.g., ΔH_{mix} may be of different signs for compatible and incompatible elements). Third, the model can
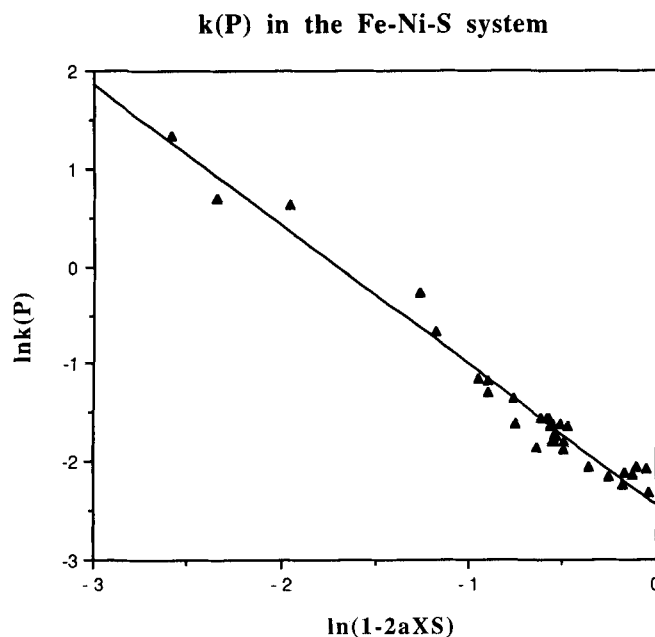
k(P) in the Fe-Ni-S system

Fig. 4—Ln k(P) vs ln $(1 - 2\alpha X_S)$. Although not a metal, P appears to behave in the same manner as Ni, Ge, and Ir. The k values span a range of ~40.
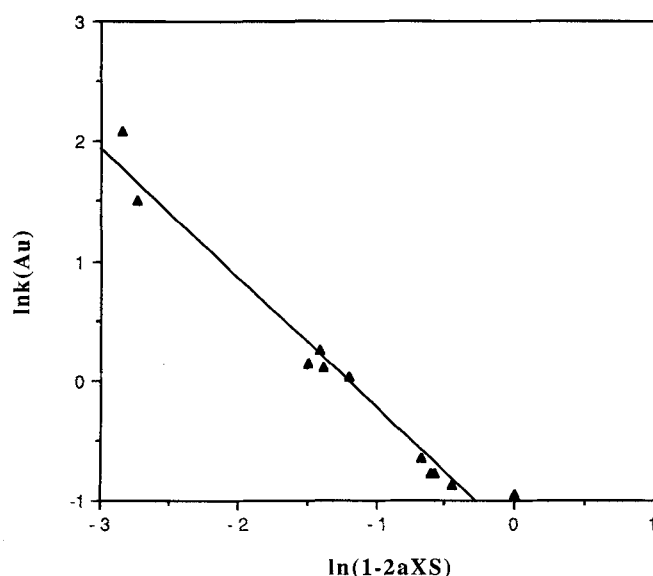
k(Au) in the Fe-Ni-S system

Fig. 5—Ln k(Au) *vs* ln $(1 - 2\alpha X_S)$.

k(Co) in the Fe-Ni-S system

Fig. 7—Ln k(Co) *vs* ln $(1 - 2\alpha X_S)$.

predict changes in k(Cr), which decreases, rather than increases, with increasing S in the liquid. All of these observations are consistent with a model in which interactions of nonmetals in the metallic liquid are of paramount importance, while other effects, such as temperature and γ_E^{Solid}, are secondary.

Finally, we have performed a simple test to evaluate the relative importances of temperature, activity coefficient of the solid, and the composition of the liquid. To the extent that either ideal or nonideal effects in the solid are important, there will be a change in ln (k) that (if ΔH is constant) will go as $1/T$ (*i.e.*, an Arrhenius diagram). We have parameterized changes in liquid composition as $(1 - n\alpha X)$. Thus, to compare these various effects, we have regressed ln k(Ge) *vs* $1/T$, *vs* $(1 - 2\alpha X_S)$,

and *vs both* $1/T$ and $(1 - 2\alpha X_S)$. The regression of ln k(Ge) with $1/T$ yields a correlation coefficient (r^2) of 0.872 and a standard error of 0.67, and the regression of ln k(Ge) and ln $(1 - 2\alpha X_S)$ has an r^2 of 0.986, with an error of 0.22. If a multiple regression of ln k(Ge) *vs* both $1/T$ and ln $(1 - 2\alpha X_S)$ is performed, there is little improvement over the simple regression *vs* ln $(1 - 2\alpha X_S)$. In the multiple regression, the r^2 increases to 0.991, and the standard error decreases to 0.18. Clearly, little is gained by including a simple $1/T$ dependence in the model. If effects other than liquid composition are to be considered, they must be more complex than the Arrhenius-type relation explored here.
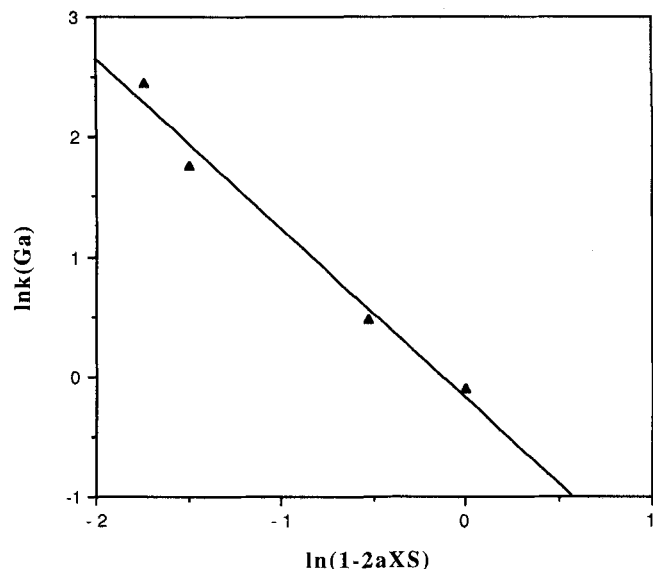
k(Ga) in the Fe-Ni-S System

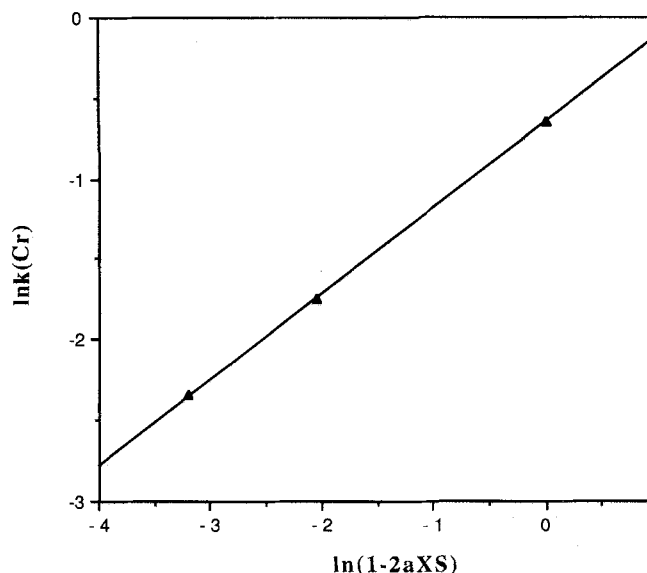Fig. 6—Ln k(Ga) *vs* ln $(1 - 2\alpha X_S)$.

k(Cr) in the Fe-Ni-S System

Fig. 8—Ln k(Cr) *vs* ln $(1 - 2\alpha X_S)$. Note the change in slope. Here, as S is added to the system, k(Cr) *decreases*, illustrating the chalcophile behavior of Cr.

Table III. Intercepts, Slopes, and Correlation Coefficients for Regressions Based on the Data in Table I

Independent Variable	Dependent Variable	Intercept $k(X_N = 0)$	Slope (β)	Correlation Coefficient	Number of Points
ln [k(P)]	ln (1 − 2αX_S)	−2.443	−1.433	0.984	34
ln [k(Cr)]	ln (1 − 2αX_S)	−0.684	0.533	1.000	3
ln [k(Co)]	ln (1 − 2αX_S)	−0.028	−0.671	0.998	4
ln [k(Ni)]	ln (1 − 2αX_S)	−0.101	−0.339	0.983	47
ln [k(Ga)]	ln (1 − 2αX_S)	−0.183	−1.419	0.991	4
ln [k(Ge)]	ln (1 − 2αX_S)	−0.547	−1.753	0.993	20
ln [k(Ir)]*	ln (1 − 2αX_S)	0.498	−2.600	0.994	11
ln [k(Au)]	ln (1 − 2αX_S)	−1.306	−1.082	0.984	11
ln [k(Ni)]	ln (1 − 4αX_P)	—	—	0	13
ln [k(Ga)]	ln (1 − 4αX_P)	−0.117	−0.508	0.975	3
ln [k(Ge)]*	ln (1 − 4αX_P)	−0.511	−0.839	0.989	8
ln [k(Ir)]	ln (1 − 4αX_P)	0.417	−1.016	0.975	6
ln [k(Au)]	ln (1 − 4αX_P)	−0.886	−0.519	0.967	6

*One point omitted from regression which appears not to have approached equilibrium. Values for α in the S- and P-bearing systems are 1.09 and 1.36, respectively.

B. Comparison with Interaction Coefficients

We can compare the results of the regressions in the Fe-Ni-S system with more traditional metallurgical measurements. In our model, at very low nonmetal contents, (∂ ln $\gamma/\partial X_S$) approaches −2$\alpha\beta_S$, which may be compared to the first-order interaction coefficient ε_E^S = (∂ ln $\gamma/\partial X_S$) reported for Fe-rich melts at 1600 °C.[6] The values are summarized in Table IV. The agreement between −2$\alpha\beta_S$ and ε_E^S is good for Ge and P, and the agreement for other elements such as Cr, Au, and Co may be acceptable. For Ir, we have compared the value of −2$\alpha\beta_S$ with that of ε_W^S = 5.1, because W segregation is similar to Ir segregation in the Fe-Ni-S system.[3] The worst agreement is for Ni, which is not a trace constituent in our system. In general, the model holds best for elements such as Ge which strongly interact with nonmetals. The agreement is less good for elements which interact more weakly with nonmetals, Ni being the best example of this behavior.

It has occurred to some reviewers that any agreement of our −2$\alpha\beta$ term with ε must be fortuitous. Our constants are determined for solutions that are not always dilute with respect to S, and they were performed over a range of temperatures that never were as high as 1600 °C. However, as we have continually pointed out, we see no

evidence that temperature is of great importance in determining γ_E^{Liquid}. Further, our α and β terms, although appropriate for solutions with high concentrations of S, also provide a good fit to the k(Ge) data taken at fairly low concentrations of S. Consequently, We regard any agreements between metallurgical interaction coefficients for Ge, Ir, and P and our −2$\alpha\beta$ terms as consistent with our model.

C. Extension to the Fe-Ni-S-P System

In order to extend the model to the more complex Fe-Ni-S-P system, the effects of the nonmetal species on the tracer element can be represented by (1 − 2$\alpha_S X_S$ − 4$\alpha_P X_P$). In the Fe-Ni-S and Fe-Ni-P systems, we have shown that the segregation coefficient for element E can be modeled, respectively, as

$$\ln k(E) = \beta_S \ln (1 - 2\alpha_S X_S) + C_S \qquad [12]$$

$$\ln k(E) = \beta_P \ln (1 - 4\alpha_P X_P) + C_P \qquad [13]$$

The nonmetal terms, (1 − 2$\alpha_S X_S$) and (1 − 4$\alpha_P X_P$), can be interpreted as defining the mole fraction of (Fe + Ni) in the metallic liquid which is not associated with a nonmetal. An extension of this reasoning to the Fe-Ni-S-P system suggests that the effective activity of (Fe + Ni) can be expressed as a function of (1 − 2$\alpha_S X_S$ − 4$\alpha_P X_P$). Thus, in the combined Fe-Ni-S-P system, the general form which we predict is

$$\ln k(E) = \beta_{SP} \ln (1 - 2\alpha X_S - 4\alpha_P X_P) + C_{SP} \qquad [14]$$

where the value of β_{SP} should be related to the values of β_S and β_P reported in Table II. One possible way of representing β_{SP} is

$$\beta_{SP} = [2X_S/(2X_S + 4X_P)]\beta_S + [4X_P/(2X_S + 4X_P)]\beta_P \qquad [15]$$

The constant C_{SP} may either also be treated as a weighted linear combination of C_S and C_P or taken to be ln k(E) in the nonmetal-free system. Equations [14] and [15] have been used to predict k values of Ge and Ni in experiments performed in the Fe-Ni-S-P system (Table II). Figures 9 and 10 show the results of these predictions.

Table IV. Comparison of Model Results with Measured Interaction Coefficients

Element	β Fe-Ni-P System	β Fe-Ni-S System	−2$\alpha_S\beta_S$	ε_E^S*
P	—	−1.433	3.1	4.1
Cr	—	0.533	−1.2	−2.2
Co	—	−0.671	1.5	0.6
Ni	0.0	−0.339	0.7	−0.1
Ga	−0.508	−1.419	3.1	—
Ge	−0.839	−1.753	3.8	4.0
Ir	−1.016	−2.600	5.7	5.1*
Au	−0.519	−1.082	2.4	0.9

*Data for tungsten from Ref. 6.

Predicted k(Ge) vs. Measured k(Ge)
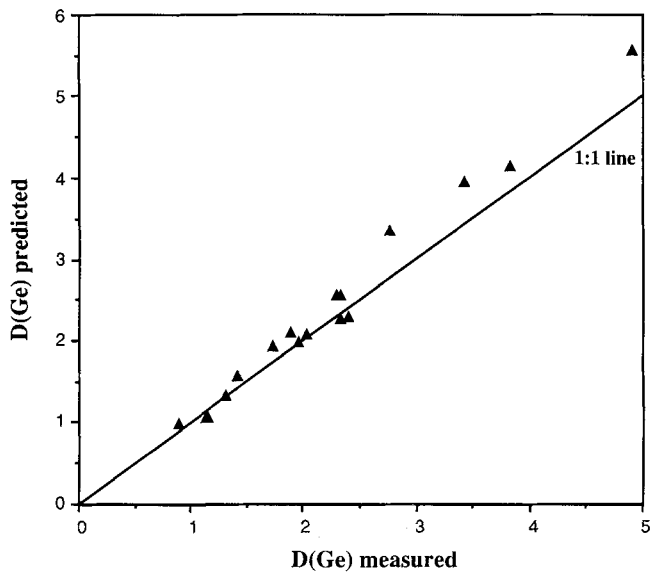

Fig. 9—$k(Ge)_{predicted}$ vs $k(Ge)_{measured}$. The values of $k(Ge)$ predicted in the Fe-Ni-S-P system from data in the Fe-Ni-S and Fe-Ni-P systems typically display a good correlation with the measured values. The line of slope 1 is for reference. Four Henry's law experiments were omitted from the figure. These experiments contained small quantities of Ge and have commensurately larger uncertainties in $k(Ge)$.

k(Ni) in the Fe-Ni-S-P system
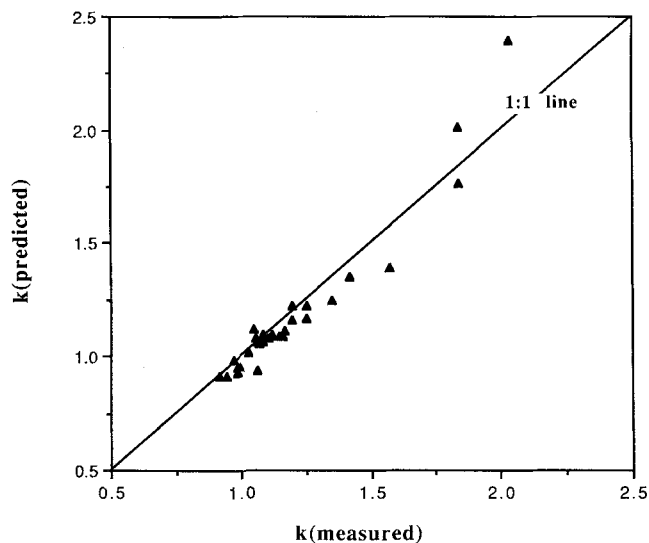
Fig. 10—$k(Ni)_{predicted}$ vs $k(Ni)_{measured}$. The values of $k(Ni)$ in the Fe-Ni-S-P system predicted on the basis of the Fe-Ni-S system are also typically in good agreement with those measured. The line of slope 1 is for reference.

With the exception of four Henry's law experiments, which contained less than 0.2 wt pct Ge in the liquid (experiments 41B, 43B, 43C, and 47C, which are not shown in Figure 9 but are listed in Table II), the predictions and the measured values agree quite well. Even $k(Ge)$ for those experiments that we have excluded was predicted to within 30 pct. Thus, the parameterizations that we have described above appear to have useful predictive powers for describing more complex systems. In

particular, the additivity of the effects of S and P reinforces our contention that the solid phase acts passively while changes in liquid composition dominate changes in $k(E)$.

IV. DISCUSSION

The success of the model in describing both simple and relatively complex systems allows us to examine the results of other experimental techniques. As we have pointed out elsewhere,[7] the application of plane front growth studies to the measurement of segregation coefficients[10,11,12] is difficult. In our own experiments, we have investigated the effects of experimental duration, oxygen fugacity, quench rate, and the concentration of the tracer, and we are confident of our technique.[7] Figure 11 shows the paths of two Sellamuthu and Goldstein experiments[11] in S vs P space as compared to several of our own experiments (triangles). Clearly, both sets of experiments cover comparable regions of composition (similarity of compositions also implies similarity in temperatures). Our equation for the change in $k(Ge)$ with changes in S and P concentration

$$\ln k(Ge) = -0.545 - \{1.753[2X_S/(2X_S + 4X_P)]$$
$$+ 0.839[4X_P/(2X_S + 4X_P)]\}$$
$$* \ln (1 - 2.18X_S - 5.44X_P) \qquad [16]$$

contrasts with that of Sellamuthu and Goldstein[11]

$$\ln k(Ge) = -0.2 + 0.09C_S - 0.9C_P \qquad [17]$$

Two aspects of the Sellamuthu and Goldstein equation are immediately apparent. First, Eq. [17] does not accurately predict the value of $k(Ge) = 0.58$ in the S and P-free system (compare a k value of 0.6 from Eq. [16]
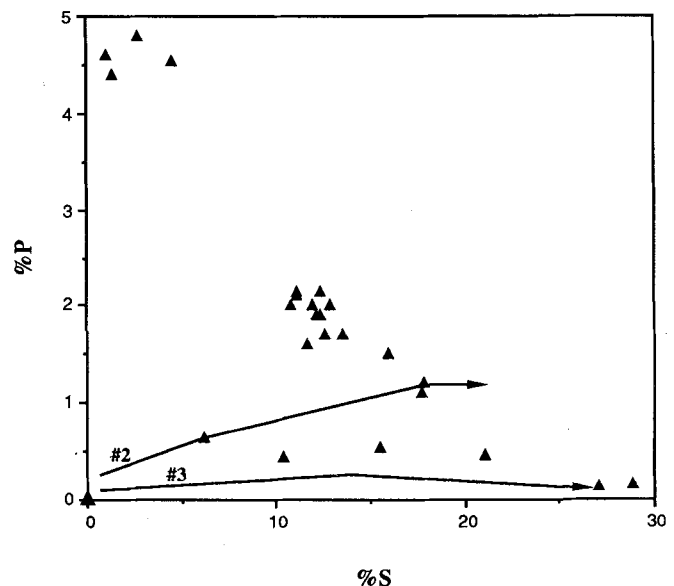

Fig. 11—Liquid P and S compositions from experiments of Ref. 7 are shown as triangles, together with the liquid evolution paths estimated by Ref. 11 for their alloys #2 and #3. Several of our experimental compositions lie in the vicinity of the liquids of Ref. 11 and allow for comparison of the two sets of data.

and 0.8 from Eq. [17]). Second, the Sellamuthu and Goldstein equation predicts that $k(Ge)$ *decreases* as P is added to the Fe-Ni-S system. This is opposite to the behavior of $k(Ge)$ in the Fe-Ni-P system and contrary to the results of our equilibrium experiments.

The issue here is whether equilibrium values of $k(E)$ can be extracted using Czochralski crystal pulling ("dynamic") techniques or whether isothermal ("static") equilibrium experiments are necessary. To the extent that $k(E)$ values can be predicted on the basis of liquid composition alone (an assumption implicit in both References 7 and 11), both sets of experiments should agree if equilibrium $k(E)$ values are extractable from the "dynamic" experiments. However, the dynamic experiments, while elegant, are not direct measurements of segregation coefficients. Rather, segregation coefficients in dynamic experiments are inferred from concentration profiles within totally solidified charges. In light of the apparent disagreement, we view the results of Sellamuthu and Goldstein with skepticism and feel that until the reasons for the discrepancy between these two types of experiments are established, the results of equilibrium experiments should be preferred. Although we have no data that are directly relevant to the experiments by Sellamuthu and Giamei on Mar-M* 200 and related alloys,[12] we

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*MAR-M is a trademark of Martin Marietta, Inc., Bethesda, MD.

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recommend that all segregation coefficients that are extracted from plane-front growth experiments be treated with caution.

V. CONCLUSIONS

We have demonstrated that simple regressions, involving only the liquid concentrations of nonmetals, are sufficient to parameterize segregation coefficients in the pseudo-ternary systems Fe-Ni-S and Fe-Ni-P. The regressions that we have presented here are simpler and more reliable than previous efforts.[1,3,7] The large changes in k values reported here and elsewhere are primarily due to variations in composition, rather than to changes in temperature or activity relations in the solid.

There are still important questions to be answered. Presently, we do not know the speciation of P in metallic liquid, and therefore, the stoichiometry coefficient that we have used in our equation (*i.e.*, 4) may not be appropriate. At low nonmetal concentrations, *any* stoichiometry coefficient will tend to yield linear regressions, and therefore, the quality of the regressions themselves provides little constraint. For this reason, it is important to measure more segregation coefficients in systems with high nonmetal concentrations. It will also be important to address partitioning in other metallic systems, such as Fe-Ni-C, to determine the range of applicability of the model.

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