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VACANCIES IN BINARY ALLOYS

Berkeley, California

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VACANCIES IN BINARY ALLOYS

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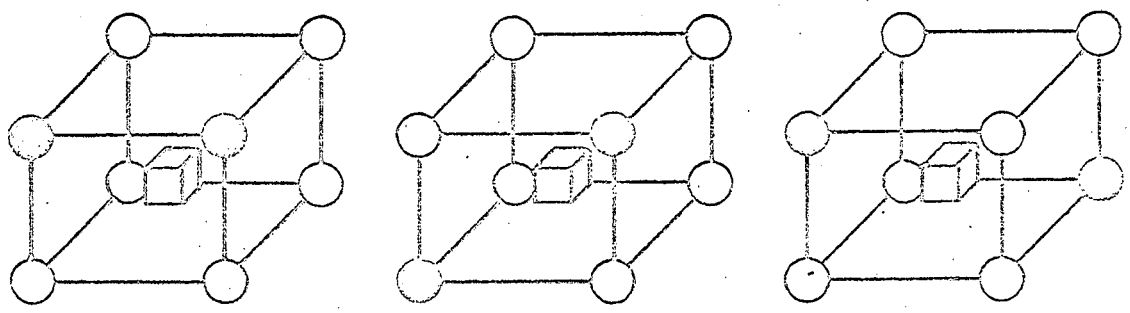
Estimates have been made of the concentration of vacancies in extremely dilute solutions.[1] A more detailed analysis will be presented here which provides an approximation that is no longer limited to extremely dilute solutions.

In a regular binary substitutioned solid solution alloy of A and B atoms let n_i be the number of vacancies coordinated with i B atoms and (z-i) A atoms such that $0 \leq i \leq z$. Thus the total number of vacancies is $n_V = \sum_{i=0}^{z} n_i$ and the total number of lattice sites is $n_S = n_A + n_B + n_V$ where n_A and n_B are the number of A and B atoms respectively in the alloy.

The free energy of formation of a vacancy g_i will be assumed to depend only on the atoms coordinated with the vacancy regardless of their arrangement on the surrounding sites. On this basis there exists z + 1 values of g_i. When i or z-i are either zero or unity, g_i is the true free energy of formation of a vacancy. But for other values of i or z-i g_i represents some average value for the various distinguishable arrangements. For example, in the body centered cubic lattice for i=2 the three types of arrangements (a,b,c) of A and B atoms about a vacancy shown in Fig. 1 are possible. As indicated, each arrangement has a unique energy of formation of a vacancy. Although such configurational effects are readily introduced into the analysis, the clarity, simplicity and utility of the analysis would suffer by the presence of an extremely large number of free energies, g_{ij}, where j identifies the configuration. Therefore, the values of g_i are taken to be appropriately weighted mean values for i or z-i other than zero or unity.

The number of ways the different types of vacancies can be distributed



a. b. c.

TYPE.
FREE ENERGY g_{2a} g_{2b} g_{2c}

A ATOMS

B ATOMS

VACANCIES

FIG. 1 ARRANGEMENTS OF 2 A ATOMS AND 6 B ATOMS ABOUT VACANCIES IN THE BODY CENTERED CUBIC LATTICE.

at random on the lattice sites is given by

$$W_1 = \frac{n_S!}{(n_S - n_V)! \prod_{i=0}^{z} n_i!} \tag{1}$$

The number of vacancies n_V will be assumed to be so few relative to n_S that the number of divacancies is negligibly small. A and B atoms will be placed at random about the vacancies in

$$W_2 = \prod_{i=0}^{z} \left\{ \frac{z!}{(z-i)!\, i!} \right\}^{n_i} \tag{2}$$

ways. Having done so the remaining A and B atoms for regular solutions can be arranged at random on the remaining lattice sites in

$$W_3 = \frac{\{n_A + n_B - z n_V\}!}{\{n_A - \sum_{i=0}^{z} n_i (z-i)\}! \{n_B - \sum_{i=0}^{z} n_i i\}!} \tag{3}$$

ways. Thus the total number of ways of obtaining the specified statistical state is given by $w = w_1 \cdot w_2 \cdot w_3$. When there are no vacancies present w reduces to the usual expression $w_R = (n_A + n_B)!/n_A!n_B!$ for random mixing of atoms.

Therefore the free energy above that for a regular solution without vacancies is

$$G = \sum_{i=0}^{z} n_i g_i - kT \ln \frac{W}{W_R} \tag{4}$$

The equilibrium number of such vacancies is then established by

$$\frac{\partial G}{\partial n_i} = 0 \tag{5}$$

consequently

$$\frac{n_i}{n_S} = \frac{z! \left\{n_A - \sum_{i=0}^{z} n_i (z-i)\right\}^{z-i} \left\{n_B - \sum_{i=0}^{z} n_i i\right\}^{i} e^{-g_i/kT}}{(z-i)!\, i! \left\{n_A + n_B - \sum_{i=0}^{z} n_i\right\}^{z}} \tag{6}$$

Since the number of vacancies is negligible relative to the number of A and B atoms, Eq. (6) is quite accurately given by

$$\frac{n_i}{n_S} = \frac{Z!}{(Z-i)!\,i!} N_A^{Z-i} N_B^{i} e^{-g_i/kT} = \theta_i e^{-g_i/kT} \tag{7}$$

where

$$(N_A + N_B)^Z = \sum_{i=0}^{Z} \frac{Z!\,N_A^{Z-i} N_B^{i}}{(Z-i)!\,i!} = \sum_{i=0}^{Z} \theta_i = 1 \tag{8}$$

and where N_A and N_B are the mole fractions of A and B atoms and θ_i the ith term of the binomial expansion of Eq. (8).

Two terms contribute to g_i, namely

$$g_i = h_i - T s_{ti} \tag{9}$$

where h_i is the enthalpy and s_{ti} is the thermal entropy for the formation of a vacancy of the ith kind. Although approximate methods for calculating h_i have been suggested,[2-8] all are known to be rather unreliable. Consequently, at present the values of h_i are best determined experimentally. On the other hand the factors contributing to s_{ti} might be estimated in terms of the change in vibrational entropy as suggested by the Einstein theory of specific heats. When an A atom is coordinated with a vacancy one degree of its vibrational frequency changes from ν_A to ν_A' where $\nu_A' < \nu_A$. Therefore the change in the thermal entropy for each A atom coordinated with a vacancy is

$$k\left\{1 + \ln \frac{kT}{h\nu_A'}\right\} - k\left\{1 + \ln \frac{kT}{h\nu_A}\right\} = k \ln \frac{\nu_A}{\nu_A'} \tag{10}$$

where h is Planck's constant and $k\{1 + \ln kT/h\nu\}$ is the Einstein thermal entropy[9] per degree of freedom. A similar expression applies for each B atom coordinated with a vacancy. Consequently for each vacancy of the ith

kind

$$s_{ti} = k(Z-i)\ln\frac{\nu_A}{\nu_A'} + k\,i\ln\frac{\nu_B}{\nu_B'} \tag{11}$$

In general s_{ti} is not expected to vary much as i changes and it will always be positive.

When $N_B = 0$, Eq. (7) reduces to the well known expression[10]

$$\frac{n_0}{n_S} = e^{-h_0/kT}\, e^{s_{t0}/k} \tag{12}$$

for the number of vacancies in a pure metal. For very dilute solutions where $0 < N_B << N_A$, it is possible to write

$$\frac{n_V}{n_S} = \sum_{i=0}^{Z}\frac{n_i}{n_S} \approx N_A^{Z}\sum_{i=0}^{Z}\frac{Z!}{(Z-i)!\,i!}\left(\frac{N_B}{N_A}\right)^{i} e^{-g_i/kT} \tag{13}$$

where the sum can be ended at that ith term where the i + 1 term is negligibly small relative to the ith term. Terminating the series at i = 1 gives a result which closely agrees with that suggested by Lomer for extremely dilute solutions.[1]

In general Eq. (7) can be written as

$$\frac{n_i}{n_S} = e^{-G_i'/RT} \tag{14}$$

where R is the gas constant and G_i' is the total free energy of formation of a mole of vacancies of the ith kind, which is given by

$$G_i' = H_i - TS_{ti} - TS_{ci} \tag{15}$$

where S_{ti} is the thermal and S_{ci} the configurational entropy per mole of vacancies and

$$\frac{S_{ci}}{R} = \ln\frac{Z!}{(Z-i)!\,i!} + (Z-i)\ln N_A + i\ln N_B \tag{16}$$

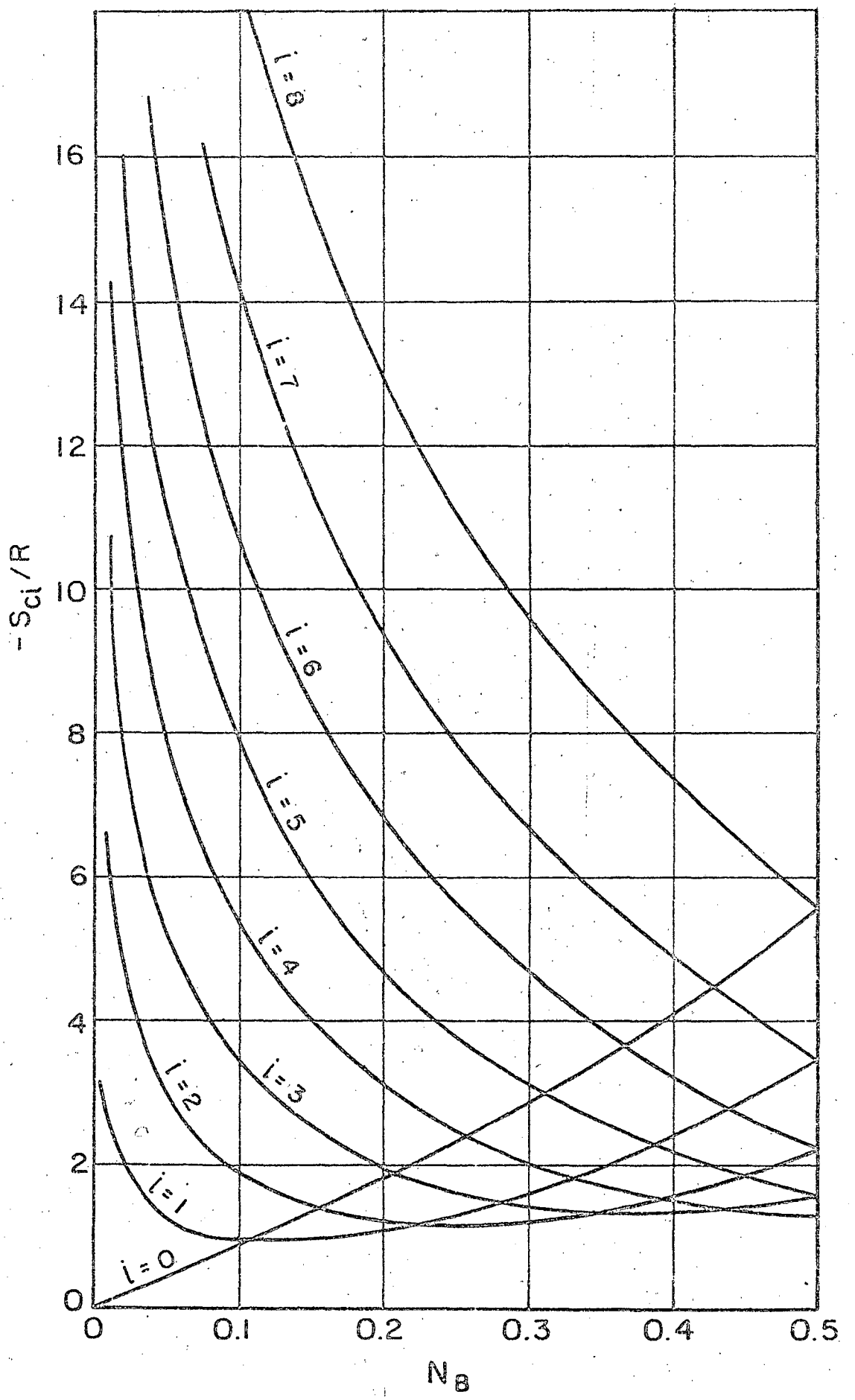


FIG. 2 CONFIGURATIONAL ENTROPY TERM FOR VACANCIES IN BODY CENTERED CUBIC BINARY ALLOYS.

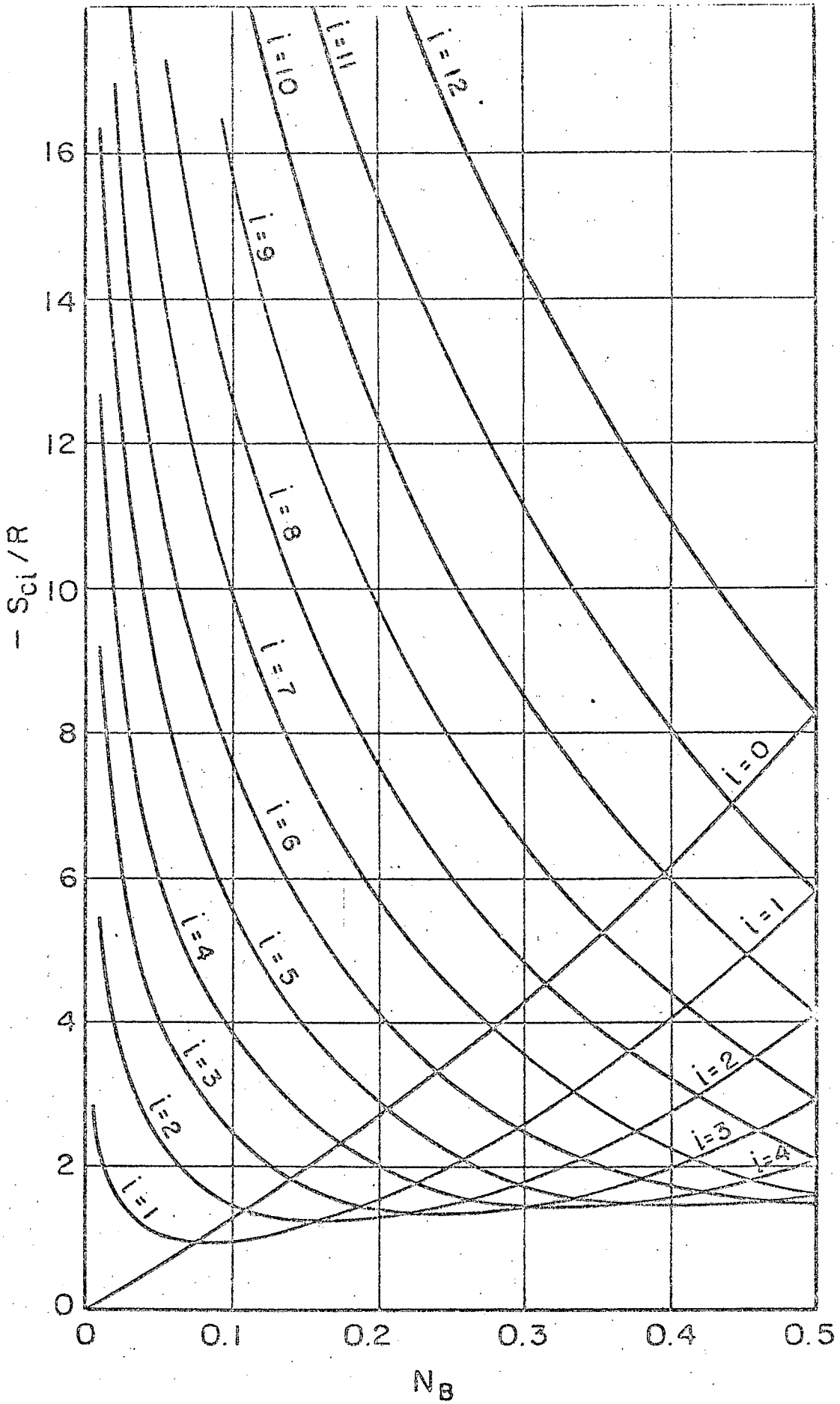


FIG. 3 CONFIGURATIONAL ENTROPY TERM FOR VACANCIES IN BINARY FACE CENTERED CUBIC ALLOYS.

ACKNOWLEDGEMENTS

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