

# A LINEAR THEORY OF THERMOCHEMICAL EQUILIBRIUM OF SOLIDS UNDER STRESS\*

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Many multicomponent solids can be represented by a continuum model. On this basis a thermodynamic theory of multicomponent stressed solids has been constructed.

After linearisation, the necessary equations for equilibrium can be separated into purely elastic and purely chemical equations. In particular, the usual Hooke's law coefficients are replaced by new open system coefficients. All the parameters of these equations can be computed from standard measurements. Examples showing the use of these formulae are presented.

## THÉORIE LINÉAIRE DE L'ÉQUILIBRE THERMOCIMIQUE DES SOLIDES SOUS L'ACTION DES CONTRAINTES

De nombreux solides à composants multiples peuvent être représentés par un modèle continu. Une théorie thermodynamique des solides à composants multiples soumis à des contraintes a été développée à partir de cette hypothèse.

Après linéarisation, les équations nécessaires pour exprimer l'équilibre peuvent être divisées en équations purement élastiques et en équations purement chimiques. En particulier, les coefficients habituels de la loi de Hooke sont ainsi remplacés par de nouveaux coefficients. Tous les paramètres de ces équations peuvent être calculés à partir des mesures classiques.

Des exemples montrant l'emploi de ces formules sont présentés.

## EINE LINEARE THEORIE DES THERMODYNAMISCHEN GLEICHGEWICHTS VON FESTKÖRPERN UNTER SPANNUNG

Viele Mehrkomponenten-Festkörper können durch ein Kontinuumsmodell dargestellt werden.

Nach der Linearisierung können die erforderlichen Gleichgewichts-Gleichungen in rein elastische und rein chemische Gleichungen separiert werden. Insbesondere werden die üblichen Koeffizienten des Hookeschen Gesetzes durch neue Koeffizienten eines offenen Systems ersetzt. Alle Parameter dieser Gleichungen können aus den Ergebnissen von Standardmessungen berechnet werden. Es werden Beispiele für die Anwendung dieser Formeln diskutiert.

## I. HISTORICAL SURVEY AND OUTLINE OF THE ARTICLE

The thermodynamic equilibrium of multicomponent stressed solids has attracted interest for the last hundred years. Gibbs<sup>(1)</sup> wrote a section of his memoir, "The Equilibrium of Heterogeneous Substances," on the subject, but he never considered a solid which can change composition while remaining in the solid state. This is not surprising since solid state diffusion was discovered only around 1894.<sup>(2)</sup> There is one notable exception: the very special case of the "solid which absorbs fluids," a material in essence comparable macroscopically to a sponge or microscopically to a gelatine (Ref. 1, pp. 215-218, 3).

The subject was reexamined much later by workers in three branches: fibers and polymers,<sup>(4-14)</sup> geology<sup>(15-32)</sup> and metallurgy.<sup>(33-39)</sup> Since their physical description of a solid—often implicit in their articles—is influenced by the material they were interested in, the various thermodynamics constructed do not reach the same results, although most claim to be general.

In light of this difficulty, this article has been written as follows: the first section is entirely devoted

to the physical description of a solid for which a thermodynamics is constructed, and to the mathematical translation of this description. Then general conditions of equilibrium are deduced. Finally, the last section is devoted to the practical use of these formulas, where a completely linear theory is worked out for actual examples.

## II. THE NETWORK MODEL OF A SOLID

The object of this study is to develop a thermodynamics of a multi-component solid which reaches equilibrium under non-hydrostatic stress. It is clear that no equilibrium is possible if the solid behaves as a viscous fluid capable of continued deformation as long as the non-hydrostatic stress persists. It is equally clear that equilibrium is possible for the purely elastic solid in which all relative motion of the atoms, whether by slip or diffusion, is proscribed. We wish to explore equilibrium under much less restrictive conditions. For a solid to reach equilibrium, we shall show that it is sufficient to require that it possess an energy density that is a single valued function of entropy density and other state variables to be identified later, and that such a requirement is realistic for a large class of solids.

The composition variables require no special attention, but the geometric variables are the main problem. For gases and liquids usually only hydrostatic

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equilibrium is possible and the volume is a sufficient variable. For non-diffusing and elastic solids one can define a strain which plays this rôle. But for diffusing solids, this is usually not so. Indeed, let us consider a small element of volume attached to the solid. During a deformation this element can be followed; but if diffusion occurs, its boundaries become "diffuse". It loses its physical identity and cannot be followed. Therefore, one cannot in general define a displacement, and hence a strain. Truesdell's<sup>(40)</sup> approach was to consider the solid composed of as many continuous media as there were independent components. But this formulation includes also cases where there is no restriction on the movement of atoms—except, maybe, kinetic ones—a situation not unlike that of a fluid. In most of these cases only hydrostatic equilibrium will be possible. The introduction of restrictions on the atomic movements eliminates those cases and allows a simpler description which still covers a large fraction of the solids we are dealing with.

We assume that the solid possesses the following property: that there exists a certain identity which we shall call network, which is embedded in the solid, and permits the definition of a displacement and hence a strain. Moreover, we shall consider only solids for which the displacement gradient (or the strain), the composition variables and the entropy density form a complete set of state variables. This has some important practical consequences. We shall identify later a stress with the derivative of the energy density with respect to strain. Therefore, on an equilibrium surface in the state space, the local stress in the solid is *uniquely* determined by the local strain, composition and entropy density (or temperature). This automatically excludes materials for which the stress is history dependent, like plastic or elasto-plastic materials. But it can include some viscoelastic solids or materials for which a restricted diffusional creep occurs.

Before developing further consequences of this approach, it may be worthwhile to give examples of solids where the network is clearly present and has the desired property. Gibb's "solid which absorbs fluid" is one of them and is exemplified by wood which absorbs water and which will reach a reversible equilibrium under non-hydrostatic stress. Here the network is the wood structure itself which is reversibly strained by the absorption of water or by stress. In interstitial solid solutions, the network is the matrix lattice itself. This case has, in III-b, been formally related to Gibb's "solids which absorb fluids" for deformations that permit unrestricted

diffusion of the interstitial atoms but permit only elastic strains of the lattice. Silicate network glasses below their softening point but at temperatures in which the positive ions can migrate, polymeric materials that absorb solvents or plasticizers and ion exchange resins all can be described by networks.

Of particular interest to metallurgists are substitutional solid solutions in which atoms diffuse by a vacancy mechanism. Here the lattice is preserved and can serve as the network, regardless of whether atoms or vacancy occupy an atomic site. The lattice can only be altered at internal or external surfaces or at dislocations by vacancy creation or annihilation there or by slip or climb. Away from these defects, the lattice remains intact and fits our requirements for a network. Vacancy coalescence into a new dislocation loop or new void is usually a rare event; and when it occurs, will be considered herein together with dislocations and free surfaces as regions where the network is not preserved.

For all these cases the lines or surfaces where the network can be diminished, increased or altered require special attention; and special examples of this will be developed.

### III. THE GENERAL CONDITIONS OF EQUILIBRIUM

The material for which we want to determine the conditions of equilibrium is composed of several phases, separated by interfaces. Within each solid phase there can be internal surfaces and dislocation lines. We require only that the physical properties are piece-wise continuous functions of position and that the discontinuities in properties coincide in position with the interfaces, surfaces and dislocations. We also neglect capillarity. These dislocation lines and surfaces act only as mathematical lines or surfaces where the network can be altered; they are otherwise without influence upon the contiguous material.

Since the type of solids and the presence of surfaces of discontinuity inside our systems give rise to different conditions of equilibrium, several cases are treated separately.

For each solid, a reference state for displacement is chosen. It is taken stress free and homogeneous.\* Orthonormal basis vector and cartesian tensors are used throughout this article. The definitions of symbols and operations are given in the appendix. Small strain theory is assumed sufficient, so that, if  $\mathbf{x}'$  is the position of a solid particle (in the continuum

\* This state might be a non-real one (cf. Gibbs Ref. 1 p. 201).

mechanical sense),  $\mathbf{x}$  its position in the actual configuration and  $\mathbf{u}$  defined by

$$\mathbf{x} = \mathbf{x}' + \mathbf{u} \quad (1)$$

the components of the strain tensor  $E$  are

$$E_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j'} + \frac{\partial u_j}{\partial x_i'} \right). \quad (2)$$

In small strain theory the difference between the derivatives  $(\partial u_i / \partial x_j')$  and  $(\partial u_i / \partial x_j)$  is neglected.

The total internal energy and total entropy are given respectively by the integral of the internal energy density  $\varepsilon'$  and the entropy density  $\mathcal{S}'$ , measured per unit volume in the reference state.

$$\mathcal{E} = \int_{v'} \varepsilon' dv' \quad (3)$$

$$\mathcal{S} = \int_{v'} \mathcal{S}' dv'. \quad (4)$$

As we have assumed in the preceding paragraph, the energy density is given by

$$\varepsilon' = \varepsilon'(E, \mathcal{S}', \rho_I', \dots, \rho_N'), \quad (5)$$

where  $\rho_I'$  is the molar density of component  $I$  per unit volume in the reference state. This equation is sometimes called caloric equation of state.<sup>(41,42)</sup>

#### (a) Internal equilibrium of an interstitial solid solution

Our interstitial solid solution contains one component which is free to move, so that its density  $\rho'$  per unit volume in the reference state is arbitrary, and a network, immobile except for small displacements due to stress.

The solid is isolated in a fixed volume (boundary condition of place of elasticity theory).

As usual in thermodynamics, its equilibrium state minimizes the energy at constant entropy. This can be expressed by the following variational problem:

$$\text{Minimum} \int_{v'} \varepsilon' dv'. \quad (6)$$

Subject to

1. Constant entropy

$$\mathcal{S} = \int_{v'} \mathcal{S}' dv' = \text{constant}, \quad (7)$$

2. Constant mass of the mobile component

$$M = \int_{v'} \rho' dv' = \text{constant}. \quad (8)$$

The first variation of the energy is:

$$\delta \mathcal{E} = \int_{v'} \left( \frac{\partial \varepsilon'}{\partial E} : \delta E + \frac{\partial \varepsilon'}{\partial \mathcal{S}'} \delta \mathcal{S}' + \frac{\partial \varepsilon'}{\partial \rho'} \delta \rho' \right) dv'. \quad (9)$$

Subject to

$$\int_{v'} \delta \mathcal{S}' dv' = 0 \quad (10)$$

$$\int_{v'} \delta \rho' dv' = 0 \quad (11)$$

The first term in equation (9) is transformed, with the divergence theorem and the identity

$$\text{div} (A \cdot \mathbf{v}) = (\text{div} A^T) \cdot \mathbf{v} + \text{tr} (A \cdot \nabla \mathbf{v}) \quad (12)$$

where  $A$  is a second order tensor,  $\mathbf{v}$  a vector and the subscript  $T$  is the operator "transpose", into

$$\begin{aligned} \int_{v'} \frac{\partial \varepsilon'}{\partial E} : \delta E dv' &= \int_{v'} \text{tr} \left[ \left( \frac{\partial \varepsilon'}{\partial E} \right)^T \cdot \delta E \right] dv' \\ &= \int_{\partial v'} \hat{n}' \cdot \left( \frac{\partial \varepsilon'}{\partial E} \right)^T \cdot \delta \mathbf{u} ds' \\ &\quad - \int_{v'} \text{div}' \left( \frac{\partial \varepsilon'}{\partial E} \right) \cdot \delta \mathbf{u} dv'. \end{aligned} \quad (13)$$

In these expressions,  $\hat{n}'$  is a unit normal on the boundary  $\partial v'$  of  $v'$  oriented toward the exterior and "div'" is a notation for the divergence operator on coordinates in the reference state, to differentiate with "div", the divergence operator on the coordinates in the actual state.

Two Lagrange multipliers  $\theta$  and  $\mu$  are introduced. In view of the small strain approximation, one gets the following necessary equilibrium conditions:

$$\text{div}' \left( \frac{\partial \varepsilon'}{\partial E} \right) \simeq \text{div} \left( \frac{\partial \varepsilon}{\partial E} \right) = 0 \quad (a)$$

$$\theta = \frac{\partial \varepsilon'}{\partial \mathcal{S}'} \quad (\text{constant throughout the volume}) \quad (14) \quad (b)$$

$$\mu = \frac{\partial \varepsilon'}{\partial \rho'} \quad (\text{constant throughout the volume}). \quad (c)$$

Since, at constant composition, the material is an ordinary elastic material,  $(\partial \varepsilon / \partial E)$  can be identified with the Cauchy stress tensor  $T$ .

With the following identities:

$$\begin{aligned} \left( \frac{\partial \varepsilon'}{\partial \mathcal{S}'} \right)_{E, \rho'} &\equiv \left( \frac{\partial \varepsilon}{\partial \mathcal{S}} \right)_{E, \rho} \\ \left( \frac{\partial \varepsilon'}{\partial \rho'} \right)_{E, \mathcal{S}'} &\equiv \left( \frac{\partial \varepsilon}{\partial \rho} \right)_{E, \mathcal{S}} \end{aligned} \quad (15)$$

equations (14) look similar to the usual equilibrium equations for fluids. Indeed, equation (14-b) indicates that the temperature of the material is constant. But, as will be shown in Section III-c, (14-a and c) in general give rise to non-homogeneous stress and composition fields.

(b) *Equilibrium between a substitutional binary solid solution and a liquid in which it is soluble*

In this section we will do two things that could have been done separately: (1) introduce our network model of a substitutional solid solution and compute the internal equilibrium condition and (2) introduce the liquid-solid boundary as an example of the surfaces or lines along which the network can be increased, decreased or altered (plastically deformed) and compute the surface equilibrium conditions. We introduce both together to demonstrate that the variational statement permits a clean separation into conditions for internal equilibrium and boundary equilibrium.

Our model of a substitutional solution is one in which the atoms are free to move subject to the network restriction which in this case is that the lattice remain intact everywhere within the solid. This places a restriction on the molar densities  $\rho_i^s$  in the reference state of the solid.

$$\rho_1^s + \rho_2^s + \rho_3^s \dots = \text{constant}. \quad (16)$$

Vacancies can be considered as one of the components but are neglected since they are usually present in dilute concentration. This condition (equation 16) constitutes a constraint and offers no special difficulty in the variation calculation. It is similar to constraints found for chemical compounds and electrolytic solutions. For a binary solution it becomes

$$\rho_1^s + \rho_2^s = \text{constant}. \quad (16a)$$

The fluid is described in a parallel manner (cf. Gibbs, p. 105 *et seq.*, equation 147) by an energy density  $\epsilon^F$ , function only of  $\mathcal{A}^F$  and  $\rho_1^F, \rho_2^F$ . This description is different from the usual, but is entirely equivalent and allows better comparison with the solid.

The system is isolated in a fixed volume, and its total energy is:

$$\mathcal{E} = \mathcal{E}^s + \mathcal{E}^F$$

$$\mathcal{E} = \int_{v'} \epsilon^s dv' + \int_v \epsilon^F dv.$$

Note that integration is performed on the reference volume for the solid, but on the actual volume for the fluid. Superscripts have been omitted on each

volume of integration and will be omitted, to simplify the notation, each time there is no ambiguity. The first variation of the energy of the solid is:

$$\delta \mathcal{E}^s = \int_{v'} \left( \frac{\partial \epsilon^s}{\partial E} : \delta E + \frac{\partial \epsilon^s}{\partial \mathcal{A}^s} \delta \mathcal{A}^s + \frac{\partial \epsilon^s}{\partial \rho_1^s} \delta \rho_1^s + \frac{\partial \epsilon^s}{\partial \rho_2^s} \delta \rho_2^s \right) dv' + \int_s \epsilon^s \delta \mathbf{x}^s \cdot \hat{n}^s ds. \quad (17a)$$

The surface integral is due to accretion and dissolution of solid and is computed on the surface  $s$  in the actual state.  $\hat{n}^s$  is the normal pointing from the solid toward the fluid.

The first variation of the fluid is:

$$\delta \mathcal{E}^F = \int_v \left( \frac{\partial \epsilon^F}{\partial \mathcal{A}^F} \right) \delta \mathcal{A}^F + \frac{\partial \epsilon^F}{\partial \rho_1^F} \delta \rho_1^F + \frac{\partial \epsilon^F}{\partial \rho_2^F} \delta \rho_2^F \right) dv + \int_s \epsilon^F \delta \mathbf{x}^F \cdot \hat{n}^F ds. \quad (17b)$$

The total first variation is subject to the conditions due to conservation of total entropy, total mass of component and the network condition in the solid:

$$\begin{aligned} \int_{v'} \delta \mathcal{A}^s dv' + \int_s \mathcal{A}^s \delta N^s ds \\ + \int_v \delta \mathcal{A}^F dv - \int_s \mathcal{A}^F \delta N^F ds = 0 \\ \int_{v'} \delta \rho_1^s dv' + \int_s \rho_1^s \delta N^s ds \\ + \int_v \delta \rho_1^F dv - \int_s \rho_1^F \delta N^F ds = 0 \quad (18) \\ \int_{v'} \delta \rho_2^s dv' + \int_s \rho_2^s \delta N^s ds \\ + \int_v \delta \rho_2^F dv - \int_s \rho_2^F \delta N^F ds = 0 \\ \delta \rho_1^s + \delta \rho_2^s = 0. \end{aligned}$$

The first term of equation (17a) is transformed by the divergence theorem

$$\int_{v'} \frac{\partial \epsilon^s}{\partial E} : \delta E dv' = \int_{s'} \hat{n}^s \cdot \left( \frac{\partial \epsilon^s}{\partial E} \right)^T \cdot \delta \mathbf{u} ds' - \int_{v'} \text{div}' \left( \frac{\partial \epsilon^s}{\partial E} \right) \cdot \delta \mathbf{u} dv. \quad (19)$$

In this equation use has been made of the fact that  $\delta \mathbf{u}$  is zero on the surface of the solid, except along the interface  $s'$ . The surface integral is transformed

by Nanson's formula<sup>(41)</sup> into a surface integral on  $s$ :

$$\int_s \dot{n}^s \cdot \left( \frac{\partial \varepsilon'}{\partial E} \right)^T \cdot \delta \mathbf{u} \, ds' = \int_s J^{-1} \delta \mathbf{u} \cdot \frac{\partial \varepsilon'}{\partial E} \cdot \mathbf{F}^T \cdot \hat{n}^s \, ds, \quad (20)$$

where  $\mathbf{F}$  is the displacement tensor, the components of which are

$$F_{ij} = \frac{\partial x_i}{\partial x_j'}$$

and  $J$  is its determinant.  $\delta \mathbf{u}$  on the surface is decomposed into a normal and a tangential component.

$$\delta \mathbf{u} = \delta u_n \hat{n}^s + \delta u_t \hat{t}^s$$

The continuity between solid and fluid implies that

$$\delta u_n + \delta N^s = -\delta N^F \quad (21)$$

at each point on the surface  $s$ .

Three Lagrange multipliers  $\theta$ ,  $\mu_1$ ,  $\mu_2$  are introduced to eliminate the integral constraints.  $\delta N^F$  and  $\delta \rho_2'^s$  are eliminated from the total variation of the energy with equations (18-d) and (21), so that we are left with independent variables. In view of the small strain approximation and the identification of  $\partial \varepsilon / \partial E$  with the Cauchy stress tensor, one is left with the following necessary conditions of equilibrium:

$$\text{div } \mathbf{T} = 0 \quad \text{inside the solid,} \quad (22)$$

$$\theta = \frac{\partial \varepsilon'^s}{\partial \Delta'^s} = \frac{\partial \varepsilon^F}{\partial \Delta^F} \quad \text{constant inside the overall volume,} \quad (23)$$

$$\mu_1 - \mu_2 = \left( \frac{\partial \varepsilon'^s}{\partial \rho_1'^s} \right)_{E, \Delta'^s, \rho_2'^s} - \left( \frac{\partial \varepsilon'^s}{\partial \rho_2'^s} \right)_{E, \Delta'^s, \rho_1'^s} \quad \text{constant inside the solid,} \quad (24)$$

$$\mu_1 = \frac{\partial \varepsilon^F}{\partial \rho_1^F} \quad \text{constant inside the fluid,} \quad (25)$$

$$\mu_2 = \frac{\partial \varepsilon^F}{\partial \rho_2^F} \quad \text{constant inside the fluid,} \quad (26)$$

$$\hat{t} \cdot \mathbf{T} \cdot \hat{n}^s = 0 \quad \text{on the surface } s, \quad (27)$$

$$\hat{n}^s \cdot \mathbf{T} \cdot \hat{n}^s = -(\varepsilon^F - \theta \Delta^F - \mu_1 \rho_1^F - \mu_2 \rho_2^F) \quad \text{on the surface } s, \quad (28)$$

$$\begin{aligned} \varepsilon^s - \theta \Delta^s - \mu_1 \rho_1^s - \mu_2 \rho_2^s \\ = \varepsilon^F - \theta \Delta^F - \mu_1 \rho_1^F - \mu_2 \rho_2^F \quad \text{on the surface } s. \end{aligned} \quad (29)$$

The expression

$$\pi \equiv -\varepsilon + \theta \Delta + \sum_i \rho_i \mu_i \quad (30)$$

is a scalar thermodynamic pressure which reduces to the ordinary pressure in fluids. With this identification, the last three conditions on  $s$  can be written

$$\mathbf{T} \cdot \hat{n}^s = +\pi^F \mathbf{I} \cdot \hat{n}^s \quad (31)$$

$$\pi^s = \pi^F, \quad (32)$$

where  $\mathbf{I}$  is the unit second order tensor.

Equation (32) is Gibbs's equation (385). Equation (24) underlined the fact that, in this type of solid, under non-hydrostatic stress, only the difference between two formal derivatives

$$\left( \frac{\partial \varepsilon'^s}{\partial \rho_1'^s} \right)_{\rho_2'^s, \Delta'^s, E} - \left( \frac{\partial \varepsilon'^s}{\partial \rho_2'^s} \right)_{\rho_1'^s, \Delta'^s, E}$$

has a physical significance and is constant throughout the volume.

Cases (a) and (b) can be combined, and their generalisation to multi-component solids in equilibrium with several fluids is straightforward.

Within a multicomponent solid at equilibrium under non-hydrostatic stress, equations (22) and (23) (or their equivalents 14a and b) hold. For each of the interstitial components, a chemical potential can be defined and is constant (equation 14c), while for the  $N$  substitutional components, the  $N - 1$  chemical potential differences are defined and constant (equation 24). The case of a component that is both substitutional and interstitial, or of component species that undergo chemical reaction can also be treated by the same methods.

The equilibrium between solid and fluid requires that the normal pressure be constant all along the bounding surface of a particular volume of the fluid. For a solid obeying the compatibility condition and fully enclosed by a fluid, this results in hydrostatic conditions. Non-hydrostatic conditions require either that the solid have a non-compatibility or that its surface is in contact with more than one fluid at different pressure (Gibbs, p. 196), or that part of its surface is under tractions other than those imposed by the fluid. While each of the fluids at different pressure can be in equilibrium with the same solid, they will not be in equilibrium with each other. Not only are their pressures different, but as was demonstrated by Gibbs (equations 393-5), the chemical potential of each substitutional element will be different in each of the fluids. Furthermore, as was also demonstrated by Gibbs (equation 39), each fluid is supersaturated with respect to the precipitation of a hydrostatic solid.

The case of solid-solid equilibrium will be treated in the article on non-linear theory.

(c) *The open-system elastic constants*

For practical use of the general equilibrium conditions derived above it is more convenient to make a change of variables, and to show that a detailed knowledge of the energy density function is also not necessary. It will be shown in this section that two equations of state involving no new type of measurement are sufficient to put the problem in known mathematical terms.

For simplicity, we consider again only binary substitutional and interstitial solid solutions. In the first case, the total number of lattice sites per unit volume in the reference state is constant; in the second, the total number of immobile atoms per unit volume in the reference state is constant. Let  $\rho_0'$  be in both cases this constant density. It is convenient to take as independent composition variable the ratios  $\rho_1'/\rho_0'$  or  $\rho'/\rho_0'$  which in both cases shall be called  $c$ .

For interstitial solutions, the differential of the energy density is

$$d\varepsilon' = T_{ij} dE_{ij} + \theta d\alpha' + \rho_0' \mu dc. \quad (33)$$

We shall use the same expression for a binary substitutional solution, with the understanding that

$$\mu = \left( \frac{\partial \varepsilon'}{\partial c} \right)_{\theta', E} = \left( \frac{\partial \varepsilon'}{\partial \rho_1'} \right)_{\rho_2', \theta', E} - \left( \frac{\partial \varepsilon'}{\partial \rho_2'} \right)_{\rho_1', \theta', E}. \quad (34)$$

Change of variables in the differential (33) are made as usual, and the following Maxwell relations can be deduced from equation (33) by differentiating  $\varepsilon' - T_{ij}E_{ij}$  twice with respect to  $c$  and  $T_{ij}$ .

$$\left( \frac{\partial E_{ij}}{\partial c} \right)_{T_{kl}, \theta} = -\rho_0' \left( \frac{\partial \mu}{\partial T_{ij}} \right)_{c, \theta, T_{kl} \neq ij}. \quad (35)$$

(1) *The open system—interstitial solution.* We now want to solve the following problem. A solid (interstitial solution) is in equilibrium, under hydrostatic pressure  $p$ , with a fluid in which only the interstitial component can dissolve.  $c_0$  is the composition of the solid in this state. A non-hydrostatic stress is applied on a part of the surface of the solid. The chemical potential of the mobile component and the temperature is kept constant in the fluid. When equilibrium is reached, what are the stress, strain and composition fields in the solid?

The state of the solid at  $c_0$ , under zero stress, is chosen as the reference state for measurement of the strain.

Under the general hypothesis of this article and the restrictive conditions of this case, the stress  $T$  is only function of the actual composition  $c$  and the

actual strain  $E$ , independently of the path chosen to reach this state. We choose the following paths:

1. A change of composition from  $c_0$  to  $c$  at zero stress, producing a strain  $E_c$ .

2. A change of stress from 0 to  $T$  at constant composition  $c$ . Since small strain theory was assumed applicable, and Hooke's law is valid at constant composition, the stress-strain relationship of our material is

$$T_{ij} = \mathfrak{C}_{ijkl}(E_{kl} - E_{c,kl}). \quad (36)$$

The  $\mathfrak{C}_{ijkl}$  are the usual stiffness coefficients measured at constant composition and are function of composition.  $E_c$  is also function of composition and, as will be seen (IV-2), can be computed from independent measurements. The total strain  $E$  is the measurable strain. Equation (36) is invertible into

$$E_{ij} - E_{c,ij} = \mathfrak{S}_{ijkl} T_{kl} \quad (37)$$

and the  $\mathfrak{S}_{ijkl}$  are the compliance coefficients, function of composition only.

When equations (35) and (37) are combined, one obtains the expression for the differential of the chemical potential at constant composition:

$$\rho_0' d\mu = -\frac{\partial E_c}{\partial c} : dT - \left( \frac{\partial \mathfrak{S}}{\partial c} T \right) : dT. \quad (38)$$

This equation is integrated to give:

$$\rho_0' \mu = -\frac{\partial E_c}{\partial c} : T - \frac{1}{2} \left( \frac{\partial \mathfrak{S}}{\partial c} T \right) : T + M(c), \quad (39)$$

where  $M(c)$  is an unknown function of  $c$  only. But the chemical potential under hydrostatic pressure  $p_0$  is known empirically. Equating the two expressions one obtains

$$\begin{aligned} \rho_0' [\mu(T, c) - \mu(p_0, c)] \\ = -\frac{\partial E_c}{\partial c} : (T + p_0 I) \\ - \frac{1}{2} \left( \frac{\partial \mathfrak{S}}{\partial c} T \right) : T + \frac{1}{2} p_0^2 \left( \frac{\partial \mathfrak{S}}{\partial c} I \right) : I. \end{aligned} \quad (40)$$

The pressure  $p_0$  is arbitrary and can by any convenient pressure which can simplify the problem on hand. Equations (36) and (40) are the two equations of state necessary to solve our equilibrium problem, since, as we may recall, the equilibrium conditions are

$$\text{div } T = 0 \quad (41)$$

$$\mu^s(T, c) = \mu^F(p, c^F) \quad (42)$$

where the right hand side of (42), pertaining to the fluid, is a given constant.

At this point, one can mention the difficulty of the problem since, even with linear elasticity and small strain theory, the thermodynamics included in equation (40) makes the problem highly non-linear.

However, when  $(c - c_0) = \Delta c$  is small, further linearization can be made. Let  $p_0$  equal the pressure of the fluid with which our solid is in equilibrium (i.e., we choose  $p_0$  to be  $p$ ). When the solid is at equilibrium under this pressure, one has

$$\mu^s(p, c_0) = \mu^F(p, c^F) \quad (43)$$

$\mu(T, c)$  can then be eliminated between equations (43), (42) and (40). One obtains

$$\begin{aligned} \rho_0 [\mu^s(p, c_0) - \mu^s(p, c)] \\ = - \frac{\partial E}{\partial c} : (T + p I) \\ - \frac{1}{2} \left( \frac{\partial \Xi}{\partial c} T \right) : T + \frac{1}{2} p^2 \left( \frac{\partial \Xi}{\partial c} I \right) : I. \end{aligned} \quad (44)$$

All the quantities function of  $c$  are expanded to the first order around  $c_0$ :

$$\begin{aligned} E_c &= E_1 \Delta c + O(\Delta c)^2 \\ \Xi &= \Xi_0 + \Xi_1 \Delta c + O(\Delta c)^2 \end{aligned}$$

$$\begin{aligned} \mu^s(p, c) - \mu^s(p, c_0) \\ = \frac{R\theta \Delta c}{c_0} \left[ 1 + \left( \frac{\partial \ln \gamma}{\partial \ln c} \right)_{c=c_0} \right] + O(\Delta c)^2, \end{aligned}$$

where  $\gamma$  is the activity coefficient.

At this point we introduce the notation

$$\frac{1}{\chi} \equiv \frac{\rho_0' R\theta}{c_0} \left[ 1 + \left( \frac{\partial \ln \gamma}{\partial \ln c} \right)_{c=c_0} \right]. \quad (45)$$

$\chi$  is related to the free energy per immobile site  $f$  by:

$$\frac{1}{\chi} = \rho_0' \frac{\partial^2 f}{\partial c^2} = \rho_0' \frac{\partial \mu}{\partial c}.$$

To the second order in  $\Delta c$ , equations (44) and (37) become respectively

$$\frac{\Delta c}{\chi} = E_1 : (T + p I) + \frac{1}{2} (\Xi_1 T) : T - \frac{1}{2} p^2 (\Xi_1 I) : I \quad (46)$$

$$E - \Delta c E_1 = (\Xi_0 + \Delta c \Xi_1) T. \quad (47)$$

If  $\Xi_1$  is small, so that terms containing  $\Xi_1$  can be neglected, elimination of  $\Delta c$  between equations (46) and (47) leads to:

$$E - [\chi E_1 : (T + p I)] E_1 = \Xi_0 T. \quad (48)$$

The second term of the left hand side of (48) written in terms of components, is

$$\chi E_{1ij} (T_{ij} + p \delta_{ij}) E_{1kl}.$$

It can be rearranged with the right hand side so as to group terms containing  $T$

$$E_{ij} - \chi p E_{1kl} E_{1ij} \delta_{kl} = (\Xi_{0ijkl} + \chi E_{1ij} E_{1kl}) T_{ij}.$$

More compactly written, it reads:

$$E - p \chi (\text{tr } E_1) E_1 = (\Xi_0 + \chi E_1 \times E_1) T. \quad (49)$$

The quantity  $(\Xi_0 + \chi E_1 \times E_1)$ , a fourth-order tensor, could be called the open system elastic coefficient (notation  $\Xi^*$ ).

Equation (49) contains no composition dependent terms. It is a purely elastic equation that will be written

$$E^* = \Xi^* T. \quad (50)$$

The elastic problem is now separated from the chemical problem since boundary conditions are also known and composition independent. Formally it is equivalent to an ordinary elastic problem, so that one can use already developed solutions of this problem to solve our elastic equations. Usually one has to replace  $\Xi$  by  $\Xi^*$ . Once the elastic equations are solved, the composition field is found through equation (46).

**2. The open system—substitutional system.** The problem considered is exactly the same as before, but the two components of the solid can dissolve so that the physical boundary between solid and liquid is unknown. Up to equation (39), the development is identical.

For this solid, under hydrostatic pressure  $p_0$ , the chemical potential of each of the two components (1) and (2) is known. Since under this same pressure  $\mu$  is equal to  $(\mu_1 - \mu_2)$ , it is a straightforward extension of case b. Equation (44) is now replaced by:

$$\begin{aligned} \rho_0 [\mu_1^s(p, c) - \mu_1^s(p, c_0) - \mu_2^s(p, c) + \mu_2^s(p, c_0)] \\ = - \frac{\partial E}{\partial c} : (T + p I) - \frac{1}{2} \left( \frac{\partial \Xi}{\partial c} T \right) : T + \frac{1}{2} p^2 \left( \frac{\partial \Xi}{\partial c} I \right) : I. \end{aligned} \quad (51)$$

The expressions of the two potentials  $\mu_1^s$  and  $\mu_2^s$  are

$$\begin{aligned} \mu_1^s(p, c) - \mu_1^s(p, c_0) \\ = \frac{R\theta \Delta c}{c_0} \left[ 1 + \left( \frac{\partial \ln \gamma_1}{\partial \ln c} \right)_{c=c_0} \right] \\ \mu_2^s(p, c) - \mu_2^s(p, c_0) \\ = - \frac{R\theta \Delta c}{1 - c_0} \left[ 1 + \left( \frac{\partial \ln \gamma_2}{\partial \ln (1 - c)} \right)_{c=c_0} \right]. \end{aligned} \quad (52)$$

Through the Gibbs–Duhem equation at constant pressure,

$$\frac{\partial \ln \gamma_1}{\partial \ln c} = \frac{\partial \ln \gamma_2}{\partial \ln (1 - c)}$$

$(\partial \ln \gamma_2 / \partial \ln (1 - c))$  can be eliminated, and the left hand side of equation (51) has the value

$$\frac{\rho_0' R \theta \Delta c}{c_0(1 - c_0)} \left[ 1 + \left( \frac{\partial \ln \gamma_1}{\partial \ln c} \right)_{c=c_0} \right]. \quad (53)$$

Calling again

$$\frac{1}{\chi} = \frac{\rho_0' R \theta}{c_0(1 - c_0)} \left[ 1 + \left( \frac{\partial \ln \gamma_1}{\partial \ln c} \right)_{c=c_0} \right] \quad (54)$$

it is obvious that the final equations of Section (b) are valid also in this case.

A difference, however, lies in the boundary conditions. Since the solid can dissolve in the fluid, the boundary has an unknown shape and is subject to the Gibbs' condition (32). This last equation can also be linearised, and the separation of chemical and elastic problems can again be obtained. But the elastic problem is not classical, and each particular case has to be examined. We shall leave the problem at this point.

#### IV. APPLICATIONS

In the last section, a general linear formulation has been derived. This section is concerned with the simplification brought by material symmetries, the practical calculation of the new elastic constants, and their use in a particular problem.

##### 1. The effects of material symmetries and choice of axes

The simplifications due to a particular choice of axes, or material symmetries, appear in the stress-free strain tensor and the elastic coefficient tensors.

The stress-free strain  $E_c$  and its derivative  $E_1$  at  $c = c_0$ , can always be diagonalised. Let the non-zero component of  $E_1$  be  $k_1, k_2, k_3$  when such an operation has been performed.

$$E_1 = \text{diag} (k_1, k_2, k_3).$$

Using the two indices matrix notation<sup>(43)</sup>, we see immediately (equation 49) that elastic coefficients with indices 4, 5 or 6 are unchanged, and coefficients with indices 1, 2, 3 are changed as follows:

$$\begin{aligned} \mathfrak{E}_i^* &= \mathfrak{E}_{0,ij} + k_i k_j \chi & i \text{ and } j &= 1, 2, 3 \\ \mathfrak{E}_{ij}^* &= \mathfrak{E}_{0,ij} & i \text{ or } j &= 4, 5, 6 \end{aligned} \quad (55)$$

If the set of axes that makes  $E_1$  diagonal coincides with the crystal axes, the  $\mathfrak{E}_{0,ij}$ 's simplify according to the appropriate symmetries. Formulae (55) show also that some combinations of elastic coefficients remain unchanged under certain crystal symmetries. For instance in cubic and hexagonal crystals,  $k_1 = k_2$  and the difference  $(\mathfrak{E}_{11} - \mathfrak{E}_{12})$  is unaltered.

In isotropic, cubic and occasionally in other systems a change in composition at zero stress produces a pure dilation.  $E_c$  is then a spherical tensor

$$E_c = k(c)I, \quad (56)$$

as well as  $E_1$

$$E_1 = k_1 I. \quad (57)$$

This constant  $k_1$  is identical to the constant  $\eta$  used by Cahn.<sup>(44)</sup> The change in composition and elastic equations are then given by:

$$\frac{\Delta c}{\chi} = k_1(\text{tr } T + 3p) + \frac{1}{2}(\mathfrak{E}_1 T):T - p^2(\mathfrak{E}_1 I):I \quad (58)$$

$$E_{ij} - 3p\chi k_1^2 \delta_{ij} = (\mathfrak{E}_0 + \chi k_1^2 \delta_{ij} \delta_{kl}) T_{kl}. \quad (59)$$

The most useful material symmetry, for practical applications, is probably isotropy. The elastic coefficients are given, in this case, by

$$\mathfrak{E}_{ijrs} = -\frac{\nu}{Y} \delta_{ij} \delta_{rs} + \frac{1}{2G} (\delta_{ir} \delta_{js} + \delta_{is} \delta_{jr}) \quad (60)$$

$\nu$  is the Poisson's ration,  $Y$  the Young's modulus and  $G$  the shear modulus. Inspection of formula (49) shows that  $E_1$  should be a spherical tensor for the material to remain isotropic. This is necessary since no phase change is allowed. Combining equations (57), (60) and (49) gives the new values of the familiar elastic coefficients as:

$$\begin{aligned} Y^* &= \frac{Y}{1 + \chi k_1^2 Y} \\ \nu^* &= \frac{\nu - \chi k_1^2 Y}{1 + \chi k_1^2 Y} \\ (\kappa^{-1})^* &= \kappa^{-1} + 9\chi k_1^2 \\ G^* &= G, \end{aligned} \quad (61)$$

where  $\kappa$  is the bulk modulus

$$\kappa = \frac{3(1 - 2\nu)}{Y}.$$

In terms of relative changes, the largest effect will usually be on the Poisson's ratio  $\nu$ . It is interesting to point out that the value of the shear modulus is unchanged and the values of  $Y$ ,  $\nu$  and  $\kappa$  are reduced.

Before computing numerical values of these changes it is necessary to know how  $E_c$  or  $E_1$  can be obtained.

##### 2. Calculation of the compositional strain tensor

In crystalline materials, the most precise experimental values of  $E_c$  are probably derived from lattice parameters measurements. The calculation is complex only for low symmetry crystals that do not have



orthogonal axes (triclinic, monoclinic and trigonal). For other crystal systems, the basis vectors undergo pure extension and constitute the principal axis of the compositional strain tensor  $E_c$ . Around the composition  $c_0$ , the lattice parameters are assumed continuous functions of  $c$ , and their values at  $c_0$  are noted.

$$a_i(c_0) = a_i^0 \quad i = 1, 2, 3.$$

The strain tensor  $E_c$  is given by:

$$E_c = \frac{1}{2} \text{diag} \left[ \left( \frac{a_1}{a_1^0} \right) - 1, \left( \frac{a_2}{a_2^0} \right) - 1, \left( \frac{a_3}{a_3^0} \right) - 1 \right]. \quad (62)$$

Since we need only  $E_1$ , the derivation of the preceding expression leads to

$$k_i = \frac{1}{a_i^0} \left( \frac{\partial a_i}{\partial c} \right)_{c=c_0} \quad i = 1, 2, 3 \quad (63)$$

with

$$E_1 = \text{diag} [k_1, k_2, k_3].$$

Another method is available when the stress-free strain tensor is spherical. In the limits of linear elasticity the trace of  $E_c$  is equal to:

$$\text{tr } E_c = 3k \simeq \frac{v - v_0}{v_0}$$

and its derivative to

$$\frac{\partial E_c}{\partial c} = \frac{1}{3v_0} \frac{\partial v}{\partial c} I,$$

but for interstitial solid solutions at zero stress,

$$c = \frac{n'}{v_0 \rho_0'}$$

so that

$$\frac{\partial k}{\partial c} = \frac{\rho_0'}{3} \bar{v}, \quad (64)$$

where  $\bar{v}$  is the partial molar volume of the interstitial component, at zero stress.

In the case of a binary substitutional solution, the derivative  $\partial v / \partial c$  is to be taken at constant number of sites ( $n_1' + n_2'$ ). Thus

$$\begin{aligned} \left( \frac{\partial v}{\partial c} \right)_{(n_1' + n_2')} &= (\bar{v}_1 - \bar{v}_2)(n_1' + n_2') \\ &= \rho_0' v_0 (\bar{v}_1 - \bar{v}_2), \end{aligned}$$

where  $\bar{v}_1$  and  $\bar{v}_2$  are the partial molar volumes of components 1 and 2 at zero stress. It implies immediately

$$\frac{\partial k}{\partial c} = \frac{\rho_0'}{3} (\bar{v}_1 - \bar{v}_2). \quad (65)$$

It might be worthwhile to emphasize that the quantities needed are macroscopic. The composition strain tensor required by this theory is a macroscopic average relating changes of dimensions between two macroscopic samples of different compositions. This is particularly evident in formulae (64) and (65). But the use of lattice parameters should not hinder the fact that they are indeed averages of individual lattice distortions.

We are now able to calculate some new elastic coefficients. But before examining these numerical values, the expressions first derived put us in a position where we can compare our results to two previous works.

If we consider the case where the compositional strain is spherical so that (64) is valid, and if we put  $p = 0$  in equation (40), one obtains:

$$\mu(T, c) = \mu(o, c) - \frac{1}{3} \bar{v} \text{tr } T - \frac{1}{2\rho_0'} \left( \frac{\partial \bar{\omega}}{\partial c} T \right) : T \quad (66)$$

This expression can be compared to equation (14) of Li *et al.*<sup>(34)</sup> Their  $\mu_H^0$  corresponds to our  $\mu(0, c)$ , the second term is identical, and their  $\bar{\omega}_H$  corresponds to the third term of equation (66). Our theory includes indeed the case treated by Li *et al.* and is in agreement with their results.

The results of equations (55), when they are applied to a cubic system ( $k_1 = k_2 = k_3$ ) are also in agreement with the results of Alefeld *et al.*<sup>(45)</sup> Their formula (15) or (28), when one makes use of the value of  $\Delta a/a$  they give on p. 340, becomes equivalent to (55).

### 3. Numerical values and orders of magnitude

Numerical values for four alloys can be found in Table 1. The values of  $k_i$  are large for all alloys. Such large values of  $k_i$  usually indicate a small solubility limit and vice versa. The change in the elastic coefficients, equal to  $\chi k_1^2$  for the three cubic alloys, is moderate. Exceptionally large values will exist near incoherent critical points and chemical spinodals where  $\chi$  approaches infinity.

As can be seen from the last column, the composition changes, which are proportional to the stress, become significant only in the range of high stress, thus justifying the linear approximation. In this range, the terms involving the pressure  $p$ —usually a pressure of 1 atm—becomes negligible.

The values of the second order terms in stress, in equation (46) are more difficult to assess because experimental data on the variations of the elastic coefficients with composition are sparse. Most of the data up to 1969 have been compiled in Landolt-Börnstein tables.<sup>(46)</sup> For dilute Fe-Al, the values

TABLE OF NUMERICAL RESULTS

Alloy, (at. %)	$k_1$ (Concentration unit) <sup>-1</sup>	$\chi \times 10^{12}$ (cm <sup>2</sup> /dyne)	$\chi k_1^2 \times 10^{13}$ (cm <sup>2</sup> /dyne)	$\frac{\Delta c / \text{tr } T}{\left( \frac{\text{cm}^2 \times \text{conc. unit}}{\text{dyne}} \right)}$
$\gamma$ -Fe, 5% C 1426°K	0.264	2.35	1.64	1.12
Al-2% Cu 723°K	-0.094	2.66	0.24	-0.35
$\alpha$ -brass 30% Zn 773°K	0.095	4.87	0.44	0.195
Zn-0.5% Cd 573°K	$k_1 = 0.117$ $k_2 = 0.117$ $k_3 = 0.24$	$S_{11}^* - S_{11}^\circ = 0.156 \times 10^{-13}$ $S_{33}^* - S_{33}^\circ = 0.66 \times 10^{-13}$ $S_{13}^* - S_{13}^\circ = 0.32 \times 10^{-13}$		

The necessary X-ray data have been taken from Pearson,<sup>(47)</sup> thermodynamic data from Hultgren.<sup>(48)</sup>

listed provide the following numbers (in cm<sup>2</sup>). The stress field, in our problem is given by dyne<sup>-1</sup>.

$$\frac{\partial \mathfrak{E}_{11}}{\partial c} = 1.49 \times 10^{-12}; \quad \frac{\partial \mathfrak{E}_{12}}{\partial c} = -0.98 \times 10^{-12};$$

$$\frac{\partial \mathfrak{E}_{44}}{\partial c} = -0.71 \times 10^{-12}$$

$$\sigma_{rr} = \sigma_{\theta\theta} = -\frac{Gb \sin \theta}{2\pi(1 - \nu^*)r}$$

$$\sigma_{r\theta} = \frac{Gb \cos \theta}{2\pi(1 - \nu^*)r} \quad (68)$$

$$\sigma_{zz} = -\frac{Gb\nu^* \sin \theta}{2\pi(1 - \nu^*)r},$$

The values to compare in equation (46) are  $E_{1ij}$  and  $\mathfrak{E}_{1ijk}T_{kl}$ . With  $E_{1ij}$  of the order of 5 to 10 per cent, the second order terms are clearly negligible up to stress levels of  $10^9$  dynes.cm<sup>-2</sup>.

For isotropic solids, as was mentioned earlier, the largest relative effect is on Poisson's ratio. A value of  $\chi k_1^2$  of  $0.5 \times 10^{-13}$ , of Young's modulus of  $10^{-12}$  dynes.cm<sup>-2</sup> and of  $\nu$  of 0.3 give rise to a change of more than 10 per cent between  $\nu$  and  $\nu^*$ . A change of sign in  $\nu$  might even occur if  $\chi k_1^2 Y$  is larger than  $\nu$ .

#### 4. Practical applications

Around a dislocation, atoms rearrange themselves so that largest ones are in tensile regions and smallest ones in compressive regions, forming what is called a dislocation atmosphere. The computation of this composition field can be done as follows. We consider a straight edge dislocation in an isotropic interstitial solution. Far away from the dislocation the stress is zero, the chemical potential is constant, and the composition is  $c_0$ .

Since the solution for the stress field around an edge dislocation in a constant composition material is:

$$\sigma_{rr} = \sigma_{\theta\theta} = -\frac{Gb \sin \theta}{2\pi(1 - \nu)r}$$

$$\sigma_{r\theta} = \frac{Gb \cos \theta}{2\pi(1 - \nu)r} \quad (67)$$

$$\sigma_{zz} = -\frac{Gb \nu \sin \theta}{2\pi(1 - \nu)r}.$$

where  $b$  is the magnitude of the Burger's vector of the dislocation at composition  $c_0$ .

Since, in the isotropic case, the composition field is given by

$$\Delta c = \chi k_1 \text{tr } T \quad (69)$$

around one dislocation it is:

$$\Delta c = -\chi k_1 \frac{2 + \nu^*}{1 - \nu^*} \frac{Gb \sin \theta}{2\pi r}. \quad (70)$$

The stored elastic free energy is now proportional to  $Gb^2/4\pi(1 - \nu^*)$ , and is thus lower than the elastic energy of the same dislocation at constant composition  $c_0$ .

The main difference between the composition field expressed in equation (70) and the one computed with purely elastic theories equation (47) lies in the factor  $(2 + \nu^*)/(1 - \nu^*)$ .

We shall consider a second example where the theory can be used. A parallelepiped of material A, of square cross-section is surrounded on four of its sides by an incompressible material B. Material A is put in contact on two opposite faces with a liquid L which it can absorb, but in which it cannot dissolve. What is the stress field and composition field in the material A at equilibrium? We assume that the pressure in the fluid is negligibly small and that A is an isotropic material.

The solution is obtained by performing the following operations:

(a) let the material absorb the liquid without constraints. It reaches composition  $c_0$ .

(b) stress the material along  $x$  and  $y$  to regain the original dimensions, at constant chemical potential. Let  $E_{xx}$  and  $E_{yy} = E_{xx}$  be the strain to be applied. The final stress is readily obtained using open system elastic coefficients as:

$$\begin{aligned} T_{xx} &= Y^*(1 - \nu^{*2})(1 + \nu^*)E_{xx} \\ T_{yy} &= T_{xx} \\ T_{zz} &= 0 \end{aligned} \quad (71)$$

and the expression for the composition field is

$$\Delta c = 2\gamma k_1 Y^*(1 - \nu^{*2})(1 + \nu^*)E_{xx}.$$

## V. DISCUSSION

The problems of developing a fundamental thermodynamics for chemical equilibrium in solids has been shown to be intimately connected with identifying the restrictions on chemical and diffusional processes that exist naturally within the solid. After defining the network structure and identifying it as a physically realistic concept for solids, we have shown that its existence in solids is a sufficient condition for reaching thermochemical equilibrium in non-hydrostatic stress fields. The existence of the network structure makes strain definable and a single valued function of stress and composition change.

The conditions for equilibrium of a solid were derived both in the interior of the solid where the network is intact and at a surface with a liquid in which the solid was soluble and where the network could be increased or diminished. The surface condition was shown to be separable from the interior conditions. The interior equilibrium placed conditions on the chemical potentials as well as on temperature and stress (equations 14 or 22-24), while the surface condition resulted in an equating of a special thermodynamic pressure between solid and fluid (equations 31 and 32). These conditions have also been derived for special cases by Gibbs, Li, Darken and Oriani, Nolfi, etc.

With the recognition that the application of stress under restrictions on the chemical potential produces composition changes and that these composition changes produce additional strains, the idea of an open system elastic constant is introduced (equation 50). It is shown to bear the same relationship to the ordinary isothermal elastic constant where instead of a constraint on the chemical potential the composition is held fixed, as the isothermal elastic constant (temperature fixed) bears to the adiabatic one (en-

tropy fixed). In the latter case, the difference is rigorously expressible in terms of macroscopic measurables. It is so also for the difference between the open system constant and the isothermal one, except that the difference is highly nonlinear at moderate stresses. A linearization applicable to small stress is given (equation 55 generally, and equation 61 for isotropic solids). All of the pertinent parameters are then identified with macroscopic measurables; in particular, the strain caused by composition change is just that and not some local distortion on the atomic level commonly used in obtaining interaction energies for statistical calculations of composition changes due to stress fields.

The magnitudes of the effect are discussed next. While interstitial solutions have the expectedly large effects, so do some substitutional solutions especially if they are not dilute and near a critical unmixing point.

All kinds of solute interaction problems at equilibrium can be solved readily by use of the open systems constant. The dislocation atmosphere is given as an example for the isotropic solution where the linear theory remains applicable. The stress field and elastic energy are given by the ordinary equations only the open system constants are used (equations 67 and 68), and the composition field is then determined from the actual stress field (equation 70). This produces at once a completely self-consistent dislocation atmosphere in contrast to the usual calculation in which the stress field of the dislocation without the atmosphere is used to calculate the composition change, but then no allowance is made for how the strains introduced by the atmosphere affect the stresses and hence again the atmosphere.

The non-linear case will be the subject of a subsequent paper. It may be worthwhile at this point to note that it retains the same equilibrium conditions and leads only to a non-linear stress-strain relation in which all the chemical parameters are still independently measurable on hydrostatic systems. Thus the non-linearity by not making approximations introduces only computational difficulty in applications while preserving the full rigor and self-consistency that thermodynamics is capable of achieving.

## NOTATIONS USED

### Tensor quantities

Notation	Component	Name
$\mathbb{C}$	$\mathbb{C}_{ijkl}$	stiffness tensor
$\mathbb{S}$	$\mathbb{S}_{ijkl}$	compliance tensor
$\mathbb{S}_1$	$\mathbb{S}_{1ijkl}$	first derivative of $\mathbb{S}$ with respect to composition

Notation	Component	Name	Notation	Meaning or components form	Nature
$E$	$E_{ij}$	total strain tensor			
$E_c$	$E_{c\,ij}$	stress-free strain tensor			
$E_1$	$E_{1\,ij}$	first derivative of $E_c$ with respect to $c$	$A \times B$	$A_{ij}B_{kl}$	4th order tensor
$F$	$F_{ij}$	deformation gradient	$\text{div}'$	divergence operator in the reference state	
$I$	$\delta_{ij}$	unit tensor	$\text{div}$	divergence operator in the actual state	
<b>Vector Quantities</b>					
$\mathbf{x}, \mathbf{y}, \mathbf{z}$		are places in the actual state			
$\hat{n}$ and $\hat{i}$		are unit vectors in the actual state			

The same quantities primed are taken in the reference state. Vectors, except  $\hat{n}$  and  $\hat{i}$ , are printed in boldface letters.

#### Scalars and scalar functions

$\mathcal{E}$	total energy
$\mathcal{S}$	total entropy
$\varepsilon$	energy density
$\mathcal{A}$	entropy density
$\rho_I$	mass density of element $I$
$\mu_I$	chemical potential of element $I$
$\theta$	absolute temperature
$c, c_I$	mole or mass fraction
$p$	pressure
$\pi$	thermodynamic pressure
$\gamma$	activity coefficient
$\chi$	definition in equation (45)
$V$	volume
$J$	determinant of $F$
$R$	gas constant
$k$	defined in equation (56)
$k_1$	first derivative of $k$ with respect to $c$ equation (57)

$a, a_i$  lattice parameter

#### Miscellaneous symbols

$v, v'$	volume of integration
$s$	surface of integration

#### Functions used

In the following formulae,  $A$  and  $B$  are second order tensors,  $\mathbf{b}$  is a vector and  $\mathfrak{C}$  is a fourth order tensor.

Notation	Meaning or components form	Nature
$A^T$	transpose of $A$	tensor
$\text{tr } A$	trace of $A$	scalar
$\det A$	determinant of $A$	scalar
$\mathfrak{C}A$	$\mathfrak{C}_{ijkl}A_{kl}$	tensor
$A \cdot B$	$A_{ik}B_{kj}$	tensor
$A \cdot \mathbf{b}$	$A_{ij}B_j$	tensor
$A:B = \text{tr } (A^T \cdot B)$	$A_{ij}B_{ij}$	scalar

Einstein summation convention is used throughout the article.

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