The Thermodynamics of Stressed Solids

By

J. C. M. LI, R. A. ORIANI and L. S. DARKEN

Edgar C. Bain Laboratory for Fundamental Research, United States Steel Corporation Research Center, Monroeville, Pennsylvania

Dedicated to Professor Dr. Carl Wagner on the occasion of his 65th birthday

With 1 figure

Abstract

The validity of the concept of a chemical potential of a component of an elastically stressed body is discussed. The existence of a chemical potential of a mobile component everywhere within a solid under a generalized stress system is demonstrated, as is also the existence of a chemical potential of an immobile component of a stressed body at appropriate interfaces. The theorem, that the work required for a closed reversible isothermal cycle is zero, is used to develop a general equation for the chemical potential. This is $\mu = \mu^0 + \overline{w} - W$, where μ^0 is the chemical potential in the unstressed state, $\overline{w}$ is the partial molar strain energy and W is the total work done on the stressed body per mole addition of the component. This relation is applied to various systems such as an interstitial solute in a solid under externally applied stresses, iron carbide precipitated in iron, and other precipitates in solid matrices. The equilibrium variation of concentration with position is evaluated for cases of inhomogeneous stress systems. The existence of a free energy function for a stressed body is demonstrated; however, it is differentiable only with respect to mobile components.

Introduction

The thermodynamics of stressed solids has attracted sporadic interest since the original work of GIBBS[1] (1876). WARBURTON[2] (1946) considered the absorption of water by rigid gels in which a non-hydrostatic stress system can develop as a result of the absorption.

---

[1] J. WILLARD GIBBS, "The Collected Works", Vol. I, Longmans, Green and Co., New York 1928.

[2] F. W. WARBURTON, Proc. physic. Soc. 58 (1946) 585.

18

Gurney[3] (1947) treated the cases of a stressed solid phase consisting of two components one of which is mobile and a pure fluid phase consisting wholly of that mobile component, and of a stressed one-component solid phase coexisting with a two-component fluid phase. Gurney applied his relations to the swelling of wood by the absorption of water. Flood[4] (1958) considered the change due to stress in the thermodynamic potential of only a one-component solid, obtaining results at variance with those of Gibbs. Callen[5] (1960) has presented formal relations between stress and various thermodynamic parameters. Yang, Horne, and Pound[6] (1962) applied Gibbs' method to the case of a mobile component in an elastic body under homogeneous stress.

The purpose of the present work is to avoid the basic assumption implicit in the work both of Callen and of Gurney—the existence of a free energy function for a stressed body such that the chemical potential of each component is the partial derivative of that function with respect to the number of moles of that component. It will be shown that in general such a function does not exist for a stressed body; notwithstanding this, Gurney's deduced relations for specific cases involving homogeneously stressed bodies are correct. Another motivation in our work is to extend the definition and the utility of the chemical potential to the case of a mobile component in an inhomogeneously stressed body. The procedure will consist of demonstrating the existence of a uniform chemical potential, μ_M, for a mobile component at equilibrium in an inhomogeneously stressed, multi-phase body, developing a way based on Moutier's theorem for the evaluation of μ_M, and applying the result to some known and some hitherto untreated situations. The range of validity of the chemical potential of an immobile component in a stressed solid will also be discussed.

Chemical Potential of a Mobile Component in a Stressed System

Let us consider a thought experiment performed on an isothermal two-component system of special type. In this two-component system

[3] C. Gurney, Proc. physic. Soc. **59** (1947) 629.

[4] E. A. Flood, Canad. J. Chem. **36** (1958) 1332.

[5] H. B. Callen, "Thermodynamics", John Wiley & Sons, Inc., New York 1961.

[6] Ling Yang, G. T. Horne and G. M. Pound, "Proceedings of a Symposium, Physical Metallurgy of Stress Corrosion Cracking, Pittsburgh 1959", Interscience Publishers, Inc., New York 1959, p. 29.

one component, M, is considered to be mobile and the other, I, immobile; an interstitial system such as that of hydrogen in iron may be considered representative. Let us now consider a unit cube (or rectangular parallelepiped) of such material and apply pressures P_x, P_y, P_z (or tensions) to it by means of a fluid in which the mobile component has a finite solubility, but which fluid has a vanishingly small solubility in the solid (alternatively the cube may be regarded as plated with a thin layer of material which is impervious to all substances involved except to the mobile component). For mechanical equilibrium, the pressures on opposite sides are equal. A two-dimensional section of the arrangement is shown in Fig. 1.
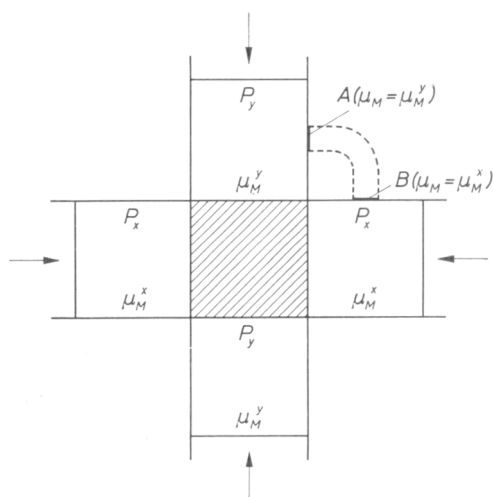

Fig. 1. Schematic of thought experiment to show uniformity of chemical potential of a mobile component in a body under stress

Clearly, at equilibrium there will develop a chemical potential, μ_M, of the mobile component in each of the fluids. The chemical potentials in the fluids at P_x, P_y and P_z are designated $\mu_M{}^x$, $\mu_M{}^y$ and $\mu_M{}^z$. Let us now introduce rigid semipermeable membranes, permeable only to the mobile component, at positions such as A and B and interconnect them with a tube filled with the same fluid (indicated by the dashed lines). It is now seen that if $\mu_M{}^x$ differs from $\mu_M{}^y$ there will be a flux of the mobile component through the tube and that by suitable means this could be made to perform work cyclicly; such an

18*

isothermal conversion of heat to work is a direct violation of the second law of thermodynamics. It follows that $\mu_M{}^x = \mu_M{}^y = \mu_M{}^z$. Since, as shown by Gibbs[1], a corresponding equality of chemical potentials does not prevail for a one-component system (nor does such an equality prevail for the immobile component of the present system) it is quite clear that a mobile component represents a special case in which its chemical potential may be regarded as a property of the uniformly stressed system since it is independent of the face on which it is measured. This has been recognized by Yang et al.[6] Clearly, a similar argument and equality prevail for each mobile component in a multicomponent system containing at least one immobile component.

It will further be observed that from any stressed solid one can always cut out a portion in such a way (the cut being always normal to any one of the principal stress axes and its surfaces in general being curved) that the initial stress state of this portion may be restored by application of normal stresses (positive or negative pressures). It is again seen by the same reasoning that the chemical potential is uniform. Since the surface may be made to pass through any two arbitrary points, and in any of the three directions normal to the principal stress axes, it follows that (at equilibrium) the chemical potential of any mobile component may be regarded as uniform throughout the system. This conclusion has also apparently been implied by Gibbs[1] if we interpret his expression "fluid component" as identical with our "mobile component".

This equality of the chemical potential of each mobile component of a stressed system is not limited to a single-phase system, for we can imagine the boundary between any two phases to be replaced by a corresponding zigzag boundary, each portion of which is normal to one of the principal stress axes. In each little segment of this boundary, we can imagine the two phases to be separated by a fluid at a definite pressure (supporting no shear). By the same type of reasoning, it then follows that the chemical potential of the mobile component is the same in each segment of the fluid. By shrinking the sizes of theses segments to infinitesimals and decreasing the amount of fluid (separation of the phases) also to an infinitesimal, it is now seen that at equilibrium the chemical potential of each mobile component is uniform throughout the stressed system, no matter how many phases (in whatever shapes) and components it may contain as long as the stresses are elastically supported.

General Equations for the Chemical Potential

Having demonstrated the existence of the chemical potential of a mobile component of a solid in any state of stress, we must next proceed to investigate the applicability and limitations of the concept of the chemical potential of any component of a stressed solid.

As a preliminary step let us consider a closed isothermal system at equilibrium. The system may consist of several components and phases. Work is done isothermally and reversibly by and upon the system in a closed cycle—for example, stresses are applied and relaxed in such a way that the system returns to its initial state. The requirement of reversibility implies that the stresses are changed so slowly that the mobile components diffuse in such a way that, at any time, departure from uniformity of the chemical potential of each is always vanishingly small; the immobile components, by definition, do not diffuse— this may usually be viewed as meaning that the distance between initially adjacent atoms changes only the small amount required by the stresses and by the composition change arising from migration of the mobile components. Since (by the first law) the energy of the system is conserved and since (by the second law) heat cannot isothermally be transformed into work, it follows that the net work done upon or by the system is zero. This may also be seen immediately by a cyclic integration of the combined first and second laws under reversible isothermal conditions

$$\oint dU = T \oint dS + \oint dW$$

where U and S are respectively the energy and entropy of the system, T is the uniform temperature and W is the work done on the system. Since the first two integrals are each zero by the first and second laws respectively, it follows that the third integral, which is the work, is also zero. This theorem has been called MOUTIER's theorem[7]. An alternative statement is that the work done in proceeding isothermally and reversibly from one state to another is independent of the path taken.

In order to apply this theorem to elastically stressed solids, we must deal with an isothermal system in mechanical equilibrium but we must consider carefully the meaning of chemical equilibrium—espe-

---

[7] E. A. GUGGENHEIM, "Thermodynamics", Interscience Publishers, Inc., New York 1949.

cially for the immobile components since the meaning of chemical potential of mobile components has already been established. We first consider a homogeneously stressed rectangular parallelepiped of uniform composition. The stress is supported by fluids exerting pressures on the various faces as in the prior discussion of a mobile component. We now focus attention on one of these interfaces between the fluid and the stressed solid. By MOUTIER's theorem a reversible transfer of a component k from the solid to the fluid requires an amount of external work which is independent of the path. Hence an equilibrium condition can be obtained by finding two suitable different paths for this transfer.

The first path chosen is the direct transfer of δn_k mole of component k from the surface of the solid to the fluid. In case k is immobile, it will be noted that δn_k must be small even in comparison to the amount of k in the surface layer of atoms. The total work done on the body during this transfer is the elastic work designated $-W_k \, \delta n_k$, where W_k is the work done per mole addition of component k. The work done on the fluid is the work of expansion designated by $W_k^F \, \delta n_k$. The total work required for this path is $(W_k^F - W_k) \, \delta n_k$.

The second path chosen involves first the complete relaxation of the stresses (on the body, but not on the fluids) and second the transfer of δn_k from the body to the fluid, and thirdly the reapplication of the stresses on the body to their original values. The work done on the body by the relaxation is designated $-w$. After relaxation the components of the body have well defined chemical potentials, that for component k being μ_k^0. The chemical potential of k in the fluid, μ_k, differs, in general, from μ_k^0 and the work required for the transfer is $(\mu_k - \mu_k^0) \, \delta n_k$. The same work of expansion $W_k^F \, \delta n_k$ is also required. The work required for the reapplication of the stress is $w - \dfrac{\partial w}{\partial n_k} \, \delta n_k$. The total work required for this path is thus

$$\left(\mu_k - \mu_k^0 - \frac{\partial w}{\partial n_k} + W_k^F \right) \delta n_k.$$

Equating the works for the two paths we find the chemical potential of k in the fluid under pressure (or tension) at equilibrium with the solid surface under stress to be

$$\mu_k = \mu_k^0 + \frac{\partial w}{\partial n_k} - W_k. \tag{1}$$

Designating $\frac{\partial w}{\partial n_k}$ by $\overline{w}_k$, which may be termed the partial molal strain energy of component k, this relation may be rewritten

$$\mu_k = \mu_k{}^0 + \overline{w}_k - W_k. \tag{2}$$

By methods similar to those used in the discussion of a mobile component, the reasoning of the foregoing paragraphs is readily extended to a general state of non-uniform stress and also to non-uniformity of the ratios of the compositions of the *immobile* components. Hence Eq. (2) is quite generally valid for any external surface area finite or infinitesimal, providing it is normal to one of the principal stress axes.

In the unstressed or the stressed state, it is now convenient to define the chemical potential of k on the surface of the solid as identical with that, μ_k, of k in the fluid in equilibrium with that surface.

Although one usually measures the chemical potential at an external surface, one may equally well be interested in the chemical potentials at an interface such as the boundary separating a precipitate (β-phase) from the matrix (α-phase). If this boundary is such that it is everywhere normal to one of the principal stress axes, one may imagine the two phases to be separated by a thin film of fluid. At equilibrium, Eq. (2) applies to both phases in contact with the fluid and we see immediately that $\mu_k{}^\alpha = \mu_k{}^\beta$ at any point on the boundary. Reducing the film of fluid to a vanishingly small thickness, we see that μ_k is a property of the interfaces of both phases. Thus we see that at any boundary (real or imaginary) normal to one of the principal stress axes or at any boundary whatsoever which may properly be replaced by a segmented boundary fulfilling this condition, the chemical potential may be given meaning in accord with Eq. (2). Equilibrium with respect to any component may be said to prevail when its chemical potential is the same on both sides of the boundary.

1. Chemical Potential of Immobile Components

Eq. (2) is a general definition of the chemical potential which can be applied to both mobile and immobile components of a body. For immobile components, since the addition or the removal of the component must take place at or from an external or internal interface

of the body, the chemical potential can be considered only as a surface property. It can be defined at any point on any interface normal to a principal stress axis. The value of the chemical potential of an immobile component, in contrast to that of a mobile component depends on the orientation of the surface. An example of this is given by GIBBS for a one-component system. In this example, a rectangular parallelepiped of a pure substance is compressed in three mutually perpendicular directions by compressive stresses P_x, P_y and P_z respectively. The chemical potential at each of these three faces is, from Eq. (2)

$$\mu_x = \mu^0 + \overline{w} + P_x \overline{V}$$

$$\mu_y = \mu^0 + \overline{w} + P_y \overline{V} \qquad (3)$$

$$\mu_z = \mu^0 + \overline{w} + P_z \overline{V}$$

in agreement with GIBBS[1]. In Eq. (3) μ^0 is the chemical potential of the unstressed substance, $\overline{w}$ is the molal strain energy in the stressed condition, and $\overline{V}$ is the molal volume.

In general, the chemical potential of an immobile component I at a surface upon which a normal stress σ (when this is the only stress performing external work during addition or removal of component I) is applied is

$$\mu_I = \mu_I{}^0 + \hat{w}_I - \sigma \hat{V}_I \qquad (4)$$

where $\mu_I{}^0$ is the chemical potential for the unstressed solid, $\hat{w}_I$ is the partial molal strain energy, and $\hat{V}_I$ is the volume* traversed by the surface per mole addition of component I to the phase considered, all defined at the same surface. These quantities, unlike the usual partial molal ones for an unstressed phase or for a mobile component, depend on the location of the external or internal surface and therefore also must be considered only as surface properties, and will in general differ from the corresponding properties in the bulk of a stress-free body.

Although μ_I is a surface property no consideration has been given to the classical GIBBS-THOMSON effect. For small particles such an appropriate term must be added.

––––––––––

* $\hat{V}_I$ can be termed the surface partial molal volume of component I.

2. Chemical Potential of Mobile Components

Although the chemical potential of an immobile component can be defined only at the surface, this is not the case for a mobile component, as we have already shown that μ_M is uniform at equilibrium everywhere within a stressed body. Within any small portion of the stressed body the stress can be considered uniform and to have all six components, σ_i. The strain energy stored within such a small portion is

$$w = \sum_i \int_0^{\varepsilon_i} V \sigma_i \, d\varepsilon_i = \sum_i \sum_j \int_0^{\sigma_i} V \sigma_i s_{ij} \, d\sigma_j \tag{5}$$

where V is the volume of the small portion, ε_i are the six components of strain, and s_{ij} are the elastic compliances.

Hence the partial molal strain energy is

$$\overline{w}_M = \sum_i \sum_j \int_0^{\sigma_i} \left[\overline{V}_M s_{ij} + (1 - x_M) \overline{V} \left(\frac{\partial s_{ij}}{\partial x_M} \right)_{x'} \right] \sigma_i \, d\sigma_j \tag{6}$$

where $\overline{V}_M$ is the partial molal volume of the mobile component M, $\overline{V}$ is the molal volume of the solid solution and x_M is the mole fraction of component M. The x' outside the partial derivative indicates that the differentiation is taken with respect to x_M at constant ratio of all other mole fractions. The work done due to the addition of δn_M is

$$W_M = V \sum_i \sigma_i \left(\frac{\partial \varepsilon_i}{\partial n_M} \right)_{n'} = \overline{V} (1 - x_M) \sum_i \sigma_i \left(\frac{\partial \varepsilon_i}{\partial x_M} \right)_{x'} . \tag{7}$$

Eq. (6) and (7) can be substituted into Eq. (2), setting $k = M$, to obtain the chemical potential of component M.

It may be noted in passing that for a system under hydrostatic pressure, Eq. (6) reduces to

$$\overline{w}_M = - \int_{\overline{V}_M (P = 0)}^{\overline{V}_M (P = P)} P \, d\overline{V}_M \tag{8}$$

and Eq. (7) reduces to

$$W_M = - P \overline{V}_M . \tag{9}$$

Substituting Eq. (8) and (9) into Eq. (2) gives the usual expression for the chemical potential of a component of a system under hydrostatic pressure

$$\mu_M = \mu_M{}^0 + \int_0^P \bar{V}_M \, dP. \tag{10}$$

Applications to Specific Systems

1. Hydrogen in homogeneously stressed iron

We will first apply these equations to the case worked out by Yang et al.[6], that of a mobile component M in a homogeneously stressed solid in equilibrium with an environing fluid phase also containing M as a component. Hydrogen dissolved in homogeneously stressed iron can serve as a prototype.

The strain energy w, stored within the iron of relaxed volume V under uniaxial tensile stress σ is

$$w = \frac{\sigma^2 V}{2 E} \tag{11}$$

where E is the Young's modulus at the existing hydrogen concentration. The work, W_H, done on the system during the addition of δn_H to the bar of iron is

$$W_H = \sigma A \, \partial l / \partial n_H \tag{12}$$

where $\partial l / \partial n_H$ is the change of length of the bar in the direction of σ produced by the transfer of δn_H gram atom of hydrogen and A is the cross-sectional area normal to σ. Differentiating (11) with respect to n_H at constant n_{Fe}:

$$\bar{w}_H = \left(\frac{\partial w}{\partial n_H} \right)_{n_{Fe}} = \frac{\sigma^2 \bar{V}_H}{2 E} - \frac{\sigma^2 \bar{V} x_{Fe}}{2 E^2} \frac{dE}{dx_H} . \tag{13}$$

Substituting the values of W_H and $\bar{w}_H$ into (2)

$$\mu_H = \mu_H{}^0 + \frac{\sigma^2 \bar{V}_H}{2E} - \frac{\sigma^2 \bar{V} x_{Fe}}{2E^2} \left(\frac{dE}{dx_H} \right) - \sigma A \frac{\partial l}{\partial n_H} \tag{14}$$

in which $\mu_H{}^0$ is the chemical potential of the hydrogen in unstressed iron with the same hydrogen concentration. If one assumes that the dissolved hydrogen expands the lattice isotropically despite the

imposed stress, i.e., that the stress does not appreciably order the hydrogen among the available sites, then

$$\frac{\partial l}{\partial n_H} = (l/3V)\bar{V}_H = \bar{V}_H/3A\,.$$

If also σ/E is small, (14) may be simplified to

$$\mu_H = \mu_H{}^0 - \sigma\bar{V}_H/3\,. \tag{15}$$

It is seen that tension decreases the chemical potential while compression increases it. Thus tension increases the solubility and compression decreases it.

For a triaxial stress system

$$w = \frac{\sigma_x{}^2 + \sigma_y{}^2 + \sigma_z{}^2}{2E}\;V$$

$$W_H = \sum_x \sigma_x\, A_x(\partial l_x/\partial n_H)\,.$$

Substituting in (2) in implicit form,

$$\mu_H = \mu_H{}^0 - \sum_x (\sigma_x\, A_x\, \partial l_x/\partial n_H) + \bar{w}_H\,.$$

Replacing the principal stresses by pressures that may be applied by fluid phases, $\sigma_x = -P_x$, the equation becomes

$$\mu_H = \mu_H{}^0 + \frac{\bar{V}_H}{3}\,(P_x + P_y + P_z) + \bar{w}_H \tag{16}$$

using the assumption of isotropic expansion of the lattice by the dissolved hydrogen. This is identical with the relation developed by YANG et al.[6] by the method of GIBBS.

2. Graphite in ferrite

Let us next consider a spherical precipitate of graphite in ferrite. The original nucleation and growth might have occurred at a higher temperature after which the system was cooled to a temperature at which the iron is immobile. The graphite particle, however, can grow because of the mobility of the carbon in ferrite. Within isotropic

elastic behavior, the growth produces a hydrostatic pressure upon the graphite (balanced by the stress field in the ferrite) which increases as the size of the particle increases. We wish to find the chemical potential of the carbon at any value of the developed pressure. The calculation will be done in two ways, first by applying Eq. (2) and then by applying Moutier's theorem to a specific reversible isothermal cycle.

(a) By the generalized chemical potential:

Since in this case the graphite is under hydrostatic pressure, P, its chemical potential is given by Eq. (10) as

$$\mu_{gr} = \mu_{gr}^0 + \int\limits_0^P V_{gr}\, dp, \tag{17}$$

where V_{gr} is the molal volume of graphite.

(b) By a Moutier cycle:

(1) Transfer directly δn mole of carbon from ferrite of concentration c to the graphite under pressure P. Since there exists chemical equilibrium between the graphite and the stressed lattice and no external force is applied to the outside ferrite surface, the external work for this step is zero.

(2) Excise the graphite, maintaining all stresses identical by external constraints. Reversibly relax all the stresses. The work required is $-w_t$, the negative of the total strain energy.

(3) Transfer δn mole of carbon from the relaxed graphite to the relaxed ferrite; this requires external work of (δn) $RT \ln (c\gamma/c_0\gamma_0]$, where c_0 is the carbon concentration in unstressed ferrite in equilibrium with graphite and γ and γ_0 are the activity coefficients at carbon concentration c and c_0 respectively.

(4) Restress the graphite and return it to the hole in the ferrite. The work required is the strain energy $w_t - \dfrac{\partial w_t}{\partial n}\, \delta n$.

Summing up and setting equal to zero one finds

$$RT \ln \frac{c\gamma}{c_0\,\gamma_0} - \frac{\partial w_t}{\partial n} = 0$$

or

$$\mu_{gr} = \mu_{gr}^0 + \frac{\partial w_t}{\partial n} . \tag{18}$$

In order to find an explicit expression for $\partial w_t / \partial n$ independent of elasticity theory we may proceed as follows. Let V^0 and $V_h{}^0$ be respectively the relaxed volume of the graphite and of the hole. The hole can accommodate only its own volume of graphite in the relaxed condition ($P = 0$). The remaining graphite, $V^0 - V_h{}^0$, can be considered to be put into the hole in small increments each one serving to increase the pressure exerted by the ferrite. Hence, the procedure would be to take dn mole of relaxed graphite of volume $V_{gr}^0\, dn$, compress it to a pressure P and inject it into the hole. Hence, the work for each differential step is

$$dw_t = P\,V_{gr}\,dn - dn \int_{V^0_{gr}}^{V_{gr}} P\,dV_{gr} = dn \int_0^P V_{gr}\,dP,$$

and hence,

$$w_t = \int_0^{(V^0 - V^0_h)/V^0_{gr}} \int_0^P V_{gr}\,dP\,dn$$

from which

$$\frac{\partial w_t}{\partial n} = \int_0^P V_{gr}\,dP. \tag{19}$$

Hence with (19), Eq. (18) becomes

$$\mu_{gr} = \mu_{gr}^0 + \int_0^P V_{gr}\,dP$$

in agreement with Eq. (17). If now we have recourse to elasticity theory, the pressure is given by[8]

$$P = \frac{4 G_\alpha\,(V^0 - V_h{}^0)/V_h{}^0}{3 + 4\,K_\beta\,G_\alpha}$$

where G_α is the shear modulus of ferrite and K_β is the compressibility of graphite. The solubility, c, in the unstressed region of ferrite in equilibrium with the compressed graphite is therefore given approximately by:

$$RT \ln (c/c_0) = P V_{gr}. \tag{20}$$

3. Cementite in Ferrite

Before proceeding to a calculation of the chemical potential of carbon in the ferrite lattice as stressed inhomogeneously by a spherical carbide particle which has grown without diffusion of iron, it is

relevant to show that under certain conditions the pressure upon a spherical precipitate is independent of size.

Consider a β-phase precipitate particle of unstrained volume V_1 fitted into a hole in the continuous α-phase, the unstrained volume of the hole being V_2. If the volume of the α-phase is sufficiently large compared to that of the β-particle, the pressure upon the particle, from elasticity theory[8], is

$$P = \frac{4G_\alpha (V_1 - V_2)/V_2}{3 + 4K_\beta G_\alpha} . \tag{21}$$

It is seen that if the β-particle grows at constant ratio V_1/V_2, P is constant.

Cementite growing in ferrite is under constant pressure provided both that the strain is purely elastic—a condition anticipated when the particles are so small that dislocation loops are not nucleated—and that the iron atoms cannot diffuse at the temperature in question. P is maintained constant because the carbon in ferrite combines with three Fe atoms at the interface to form one molecule of Fe_3C so that

$$\frac{V_1}{V_2} = \frac{V_{cem}}{3\left(\overline{V}_{Fe}^\alpha + \frac{x_c}{1 - x_c} \overline{V}_c^\alpha\right)} .$$

We note in passing that this differs from the case of graphite in ferrite where P is not constant.

We first apply Eq. (2) to the problem of cementite in stressed ferrite. The chemical potential of the cementite under pressure P exerted by the lattice is

$$\mu_{cem} = \mu_{cem}^0 + \overline{w}_{cem} + P\overline{V}_{cem}$$

where μ_{cem}^0 is the chemical potential of cementite in the relaxed state. The chemical potential of the iron at the interface is by Eq. (4)

$$\mu_{Fe} = \mu_{Fe}^0 + \hat{w}_{Fe} + P\hat{V}_{Fe}$$

where μ_{Fe}^0 similarly is the chemical potential of the iron in unstressed ferrite and $\hat{V}_{Fe}$ is the surface partial molal volume of iron in ferrite at the interface, i.e. the increase in the volume of the compressed cementite per gram atom of iron. The chemical potential of carbon in stressed ferrite, μ_c, at equilibrium is given by

$$\mu_{cem} = 3\mu_{Fe} + \mu_c$$

[8] N. F. Mott and F. R. N. Nabarro, Proc. physic. Soc. 52 (1940) 86.

and when all phases are stress-free and equilibrated,

$$\mu_{cem}^0 = 3\mu_{Fe}^0 + \mu_c^*.$$

Therefore, combining these four equations,

$$\mu_c = \mu_c^* - 3P\hat{V}_{Fe} - 3\hat{w}_{Fe} + P\overline{V}_{cem} + \overline{w}_{cem} \tag{22}$$

where we have neglected the variation of μ_{Fe}^0 with carbon concentration since the carbon is very dilute in the ferrite. Because of interface continuity it is necessary that

$$P\overline{V}_{cem} = 3P\hat{V} \approx 3P\hat{V}_{Fe}$$

where $\hat{V}$ refers to the ferrite. Hence,

$$\mu_c = \mu_c^* + \overline{w}_{cem} - 3\hat{w}_{Fe} = \mu_c^* + \frac{\partial w_t}{\partial n} \tag{23}$$

where w_t is the total strain energy of the system and n is the number of moles of Fe_3C.

We may compare this result with that obtained directly from MOUTIER's theorem by the following cycle:

1. Directly convert δn mole of Fe_3C to $3\,\delta n$ mole of Fe and δn mole of C in solution; this requires zero work.

2. Excise the cementite and relax all the stresses; the work required is [8]

$$-w_t = \frac{2G_\alpha \overline{V}_{cem}(\Delta V/V)^2 n}{3 + 4K_\beta G_\alpha} \tag{24}$$

where n is the number of moles of Fe_3C.

3. Form δn mole of Fe_3C (at zero stress) from $3\,\delta n$ mole of Fe and δn mole of C in solution; this requires the work

$$(\mu_c^* - \mu_c)\,\delta n.$$

4. Return the cementite into the ferrite; the work necessary is

$$w_t + \frac{\partial w_t}{\partial n}\,\delta n.$$

Hence

$$\mu_c = \mu_c^* + \frac{\partial w_t}{\partial n}$$

in agreement with Eq. (23). This may be expressed as

$$\mu_c = \mu_c{}^* + \frac{2\,G_\gamma\,\overline{V}_{cem}\,(\varDelta V/V)^2}{3 + 4\,K_\beta\,G_\alpha}$$ (25)

by using Eq. (24).

Table. *Increase of solubility of spherical cementite particles in ferrite occasioned by pressure on cementite supported completely elastically by stresses in ferrite arising from the misfit*

$T°(K)$	300	400	500	600	700	800	900	1000
c/c_0	17.0	8.3	5.4	4.1	3.4	2.9	2.5	2.3

For such a dilute solution $\mu_c - \mu_c{}^*$ may be written as $RT \ln (c/c_0)$ where c is the concentration in a distant unstressed region when this region is in equilibrium with the cementite under pressure. Using the elastic constants $(G_\alpha = 11.76 \times 10^6$ psi; $1/K_\beta = 34.7 \times 10^6$ psi) given by Laszlo and Nolle[9] and taking $\varDelta V/V = 0.09$ and $\overline{V}_{cem} = 23.4$ cm³/mole of Fe_3C the ratio c/c_0 has been computed by Swartz[10] at various temperatures and is given in Table 1; the calculated pressure is 66,000 atm (970,000 psi).

Positional variation of composition in inhomogeneously stressed systems

Whenever a phase is under inhomogeneous stress one may expect a positional variation of the concentration of a mobile component at equilibrium. Using Eqs. (2), (6) and (7), one may write as the condition for $\delta\mu_M = 0$ between two points at stresses σ' and σ'' respectively,

$$RT \ln \frac{\gamma' x_M(\sigma')}{\gamma'' x_M(\sigma'')} = - [\sum_i \sum_j \int_0^{\sigma_i'} \overline{V}_M\, s_{ij}\, \sigma_i\, d\sigma_j - \sum_i \sum_j \int_0^{\sigma_i''} \overline{V}_M\, s_{ij}\, \sigma_i\, d\sigma_j]$$

$$+ [\overline{V} \sum_i \sigma_i'\, (\partial \varepsilon_i/\partial x_M)_{x'} - \overline{V} \sum_i \sigma_i''\, (\partial \varepsilon_i/\partial x_M)_{x'}]$$ (26)

where the γ's are activity coefficients and we have assumed composition-independent elastic compliances and have neglected the difference between $(1 - x_M)$ and unity for solutions very dilute in M.

To apply this to the ferrite surrounding a spherical cementite particle we will assume that the matrix is elastically isotropic and

---

[9] F. Laszlo and H. Nolle, J. Mech. Physics Solids 7, (1959) 193.
[10] J. C. Swartz, to be published.

that the expansion of the lattice by the carbon atoms is the same in all directions. Then

$$\bar{V} \sum_i \sigma_i \, (\partial \varepsilon_i / \partial x_c) = \bar{V}_c^{\,\varkappa} \, \sigma_H = 0$$

where $\sigma_H = (\sigma_x + \sigma_y + \sigma_z)/3$, and is the hydrostatic component of the stress. This component is zero because of the sphericity hypothesized for the cementite and because the cementite particle is very small compared with the ferrite matrix. Applying Eq. (26) to a point in the ferrite at a distance, r, from the center of the cementite and to a point very far away where $\sigma_i \approx 0$, we find

$$\frac{x_c\,(r)}{x_c\,(\infty)} = \exp - \left[\frac{3\,\overline{V}_c^{\,\varkappa}}{8\,G_\alpha\,RT} \left(\frac{12\,G_\alpha\,a^3\,(\Delta/a)}{r^3\,(3 + 4\,K_\beta\,G_\alpha)} \right)^2 \right] \tag{27}$$

(a is the radius of the inclusion, and Δ is the difference between the relaxed radii of inclusion and hole). For the case of Fe_3C in α-Fe, $\Delta/a \approx .03$ and $\bar{V}_c^{\,\alpha} \approx 5$ cm^3/g. atom (by analogy with the case for nitrogen[11]) so that at $600\,^\circ$K, $x_c(r)/x_c(\infty) = 0.81$; thus, there is a somewhat lower concentration of carbon in the ferrite near the interface with the spherical carbide inclusion than there is very far from the particle.

There is a much larger dependence of equilibrium concentration upon position when the term in $\Sigma\sigma_i$ in Eq. (26) does not vanish, as will be the case, for example, when the inclusion is far from spherical. Under these conditions the first term on the right of Eq. (26) becomes negligible. We may illustrate the possibilities with the aid of BHARGAVA and MCLEAN's[12] numerical evaluation of stresses in ferrite generated by laths of $Fe_{16}N_2$ having elliptical cross-sections of eccentricity of $125 : 1$. With the assumption that the expansion of ferrite by dissolved nitrogen is isotropic, Eq. (26) becomes, after dropping the first term

$$RT \, \ln \frac{x_N\,(r)}{x_N\,(\infty)} = \bar{V}_N^{\,\alpha} \, \sigma_H \, .$$

Using $\bar{V}_N^{\,\alpha} \approx 5$ cm^3/g. atom[11], and $\sigma_y = 2072$ kg/mm^2, $\sigma_x = 53.5$ kg/mm^2 and $\sigma_z = 0$ at $r = a/2$, that is, directly at the ends of the

---

[11] H. A. WRIEDT and L. ZWELL, Trans. Amer. Inst. Mining metallurg. Engr. **224** (1962) 1242.

[12] R. D. BHARGAVA and D. MCLEAN, J. Iron Steel Inst. **203** (1965) 699.

19

major axis of the cross section, one finds that $x_N(a/2)/x_N(\infty) \approx 1100$ at 600 °K. Thus, there is a very large increase in nitrogen concentration at the edge of the lath compared with the concentration far away. However, this calculation must be regarded only as a first approximation since such a large solute concentration will certainly modify the stress field and also produce a tendency towards ordering of the solutes in the stress field. These two effects will tend to reduce the calculated ratio, but probably not by an order of magnitude.

It is clear that this equilibrium segregation of solute is highly localized since the magnitude of the maximum principal stress drops off very rapidly[12] with distance from the particle. Thus, at $r = \dfrac{a}{2} + 100$ Å, the concentration has reached essentially the value at $r = \infty$. Nevertheless this equilibrium segregation may have important implications for hydrogen embrittlement, stress-corrosion cracking, and some phase-transformation phenomena.

The Free Energy Function

It would be desirable to be able to define a free energy function for a stressed body such that the chemical potential of each component k is a partial derivative of such a function with respect to the number of moles of component k. This is possible if and only if the following is a total differential,

$$\sum_k \mu_k \, dn_k, \tag{28}$$

or its equivalent,

$$\sum_k (\mu_k{}^0 + \overline{w}_k - W_k) \, dn_k. \tag{29}$$

While the first term integrates to be the free energy of the unstressed body and the second term integrates to be the total strain energy, the third term is unfortunately not integrable. This can easily be seen from the Gibbs example mentioned previously. The same stressed rectangular parallelepiped can be built up in three different ways with $P_x V$, $P_y V$, or $P_z V$ as the integrated values for the third term in the expression (29). Hence we must conclude that a free energy function does not in general exist for a stressed body such that its partial derivatives are the chemical potentials of all the components.

However, if in the expression (29), all the terms involving immobile components are left out, the third term becomes $-W_M \, dn_M$ which is then integrable since the same amount of external work would be

done no matter where or how the mobile components are added to the stressed body. Hence a free energy function exists for all the mobile components but not for the immobile components; this is

$$dF = \sum_M \mu_M \, dn_M, \tag{30}$$

or as shown by GIBBS[1] (interpreting his expression "fluid component" as synonymous with our "mobile component")

$$dU = TdS + \int_V (\sum \sigma_i \, d\varepsilon_i) \, dV + \sum \mu_M \, dn_M \tag{31}$$

where U is the internal energy and S is the entropy of the whole stressed body. For a small element of volume of the body or for a homogeneously stressed body, Eq. (31) can be written as

$$dU = TdS + V \sum_i \sigma_i \, d\varepsilon_i + \sum_M \mu_M \, dn_M. \tag{32}$$

We may now define the following functions in analogy to the usual way: the enthalpy, $H = U + V \sum_i \sigma_j \varepsilon_i$; the HELMHOLTZ free energy $A = U - TS$; the GIBBS free energy $F = H - TS$. Their exact differentials are:

$$dH = TdS - V \sum_i \varepsilon_i \, d\sigma_i + \sum_M \mu_M \, dn_M \tag{33}$$

$$dA = - SdT + V \sum_i \sigma_i \, d\varepsilon_i + \sum_M \mu_M \, dn_M \tag{34}$$

$$dF = - SdT - V \sum_i \varepsilon_i \, d\sigma_i + \sum_M \mu_M \, dn_M. \tag{35}$$

Many MAXWELL-type relations may be generated from these equations such as,

$$\left(\frac{\partial \mu_M}{\partial \sigma_i} \right)_{T, \sigma', n} = - V \left(\frac{\partial \varepsilon_i}{\partial n_M} \right)_{T, n', \sigma} \tag{36}$$

and

$$\left(\frac{\partial \mu_M}{\partial \varepsilon_i} \right)_{T, \varepsilon', n} = V \left(\frac{\partial \sigma_i}{\partial n_M} \right)_{T, n', \varepsilon} \tag{37}$$

where σ' indicates constancy of all other stress components, ε' constancy of all other strain components, n' constancy of the quantities of all other material components, and σ or ε constancy of all stresses or strains.

19*

Conclusions

There exists a chemical potential of each mobile component everywhere within a solid under any elastic stress condition, and of each immobile component of an elastically stressed solid at an appropriate interface. Moutier's theorem permits the development of a general equation for the chemical potential of a component of a stressed body; this equation has been applied to a number of problems of externally applied stress and of stresses associated with precipitates. It is shown that the solubility of Fe_3C in alpha iron is increased by the growth stress. Inhomogeneity of stress, in general, gives rise at equilibrium to inhomogeneity of concentration of mobile components. Finally, a free energy function exists for a stressed body but is differentiable only with respect to the mobile components.

Acknowledgment