COMMEMORATIVE LECTURE
BY THE THIRTY-NINTH GOLD MEDALIST OF
THE JAPAN INSTITUTE OF METALS

The Expanding Scope of Thermodynamics in Physical Metallurgy[†]

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Some recent developments in the applications of thermodynamics to problems in physical metallurgy have required adaptation that are in the inventive spirit of classical thermodynamics. Diffuse interfaces and the problems that crystal lattices pose are taken as examples.

Keywords: thermodynamics, surfaces, diffuse interfaces, surface stress, crystalline solids, stress, chemical potential, diffusion potential, vacancies, diffusional creep

I. Introduction

Thermodynamics has been called⁽¹⁾ one of “three great branches of natural science that stand apart by reason of the variety of far reaching deductions drawn from a small number of primary postulates”. Einstein⁽²⁾ wrote in his Autobiographical Notes, “A theory becomes all the more impressive, the greater the simplicity of its premises, the greater the diversity of fields it ties together, and the broader the areas of its applicability. For all these reasons, classical thermodynamics made a deep impression upon me. I am convinced that it is the only physical theory of universal applicability that, within the scope of applicability of its basic concepts, will never be overthrown. (Skeptics, take note!)” The thermodynamics so highly praised is an applied science that permits one to assert what is impossible. It also permits us to make predictions about a large set of useful empirical quantities from a smaller set of more easily acquired data, usually obtained from experiment (but increasingly in recent times from first principles). The methods of thermodynamics teach us to discover useful empirical quantities, to find precise definitions for them, and then to derive the exact relations among them that make them so useful. Because of these relations, thermodynamics can be applied to a wide range of complex situations. Its predictions are confined to these quantities and will yield little or no knowledge or understanding of other details.

As a result of this success, thermodynamics has tended to become a rigid and conventional subject. Many of the applications of thermodynamics have been formalized to

such a degree, that they can be taught as routine manipulations of tabulated data for a limited, but very important, set of problem types, such as phase equilibria. The history of thermodynamics is one of adaptation to new understanding and new applications. The deeper aspects, that so impressed Einstein, are still with us and offer the promise of greater diversity of fields and broader range of applicability.

In this talk, I want to give a simplified view of the history of the process of inventing and discovering useful and very basic thermodynamic quantities and finding relations among them, in order to present to you some present day challenges for thermodynamics in physical metallurgy. I want to emphasize the flexibility of the early inventions, and to a lesser extent, the discoveries, of forms of first law work terms that have made thermodynamics the adaptable evolving science it is. Finally I want to discuss with you two modern areas of inquiry; the consequences of an alternate definition of the work for creating surfaces and interfaces, and the problems posed by crystalline substances.

II. The Inventions of Thermodynamics

The foundations of thermodynamics were in place by the middle of the nineteenth century based on the two laws of thermodynamics as enunciated by Clausius. The first law of thermodynamics, conservation of energy, evolved from experiments in the 18th century. But the gradually enlarging understanding of the full implications of energy conservation, that began with heat and work, would in time encompass an increasing number of interconvertible forms of energy. By 1923 Lewis and Randall wrote⁽³⁾ “So, as science has progressed, it has been necessary to invent other forms of energy, and indeed an unfriendly critic might claim, with some reason,

[†] Commemorative Lecture, Annual Spring Meeting of The Japan Institute of Metals, Tokyo, March 31, 1994.

that the law of conservation of energy is true because we make it true, by assuming the existence of forms of energy for which there is no other justification than the desire to retain energy as a conservative quantity". This was written shortly after the mysterious source of the apparently inexhaustible source of energy emitted by radioactive elements was understood in terms of mass as a form of energy.

In Newtonian mechanics there is mechanical energy conservation. The interconversion of kinetic and potential energy is an important and useful concept, although Einstein⁽⁴⁾ wrote: "...I would like to point out that the division of energy into two essentially different parts, kinetic and potential energy, must be felt to be unnatural".

Originally heat and temperature were considered synonymous, and so completely different from mechanical energy that no comparison made sense. In 1762 Joseph Black introduced the idea of latent heat; heat used to melt a substance was conserved even though there was no temperature rise. Black reasoned that the heat was somehow stored in the molten substance for it could be recovered upon solidification. This implied a conservation of heat, not unlike the interconversion of kinetic and potential energy in Newtonian mechanics.

The realization that heat was a form of energy came a bit later when the conversion of mechanical energy into heat was described by Count Rumford. Mayer and Joule found the quantitative equivalence of the increment of work done $-\delta w$ to the combination of heat evolved $-\delta q$ or stored as energy with a rise in temperature dT . It was possible to write an equation to express the experimental fact that mechanical energy was easily converted to heat

$$dE = \delta q - \delta w.$$

Before heat engines demonstrated the reverse process there must have been considerable remaining doubt about the equivalence of heat and work. The limitations of heat engines in accomplishing this reverse process, the Carnot efficiency, led to an understanding of the distinction between heat and work, to the second law and to a new concept called entropy which is a measure of the degradation of energy. For the remainder of this paper, δq will be replaced with TdS whenever processes are reversible.

There are many forms of work. Those that are purely physical, pressure-volume change, elastic deformation, magnetostatic and electrostatic, can all be formulated without recourse to the nature of the material, as products of force and distance. As more and more of these work terms are added together with the heat and internal energy into a fundamental first law differential, the number of thermodynamic relations that have been derived increases even more rapidly. Many examples about the combined effects of elasticity, magnetism, and electricity on materials have been derived and are used. Including the second law yields additional relations as well as stability inequalities on heat capacities, elastic coefficient, susceptibilities, and on cross-effects, such as,

the difference between C_p and C_v , elastocaloric, magnetostrictive, and many other such effects.

Recall that the Carnot efficiency of an engine is independent of the working fluid. This is in part because the engine fluid is conserved and restored to its original condition at the end of each Carnot cycle. At this level engine thermodynamics can not tell you much about the working fluid, and the thermodynamics of the first part of the 19th century did not hold any promise for a chemist or metallurgist.

All that changed when J. W. Gibbs in a momentous paper⁽⁵⁾, published in two parts in 1875/6 and 1877/8, invented a number of forms of energy for substances and substantial surfaces. All of this discovery came within the framework of the first and second law, which Gibbs considered as his axioms.

Chemical work is an important example of an invented form of energy. The chemical potential is the key invention in adapting thermodynamics to chemical and materials problems. It was introduced by Gibbs in a first-law work term; the naked work of adding a particular chemical species to a fluid without doing any other work, i.e. at constant volume, constant amount of the other species, and without adding heat (at constant entropy). Gibbs literally opened the "engine" up in order to be able to consider the process of adding or removing "fluid", thereby letting the engine concepts and the thermodynamics of engines give him information about substances.

There are two factors in this chemical work, a clearly defined change in the amount of the i th species, dN_i , and its conjugate variable called the chemical potential μ_i . By setting their product $\mu_i dN_i$ equal to the change in energy dE at constant S , amount of all the other components, N_j , and V (here the only mechanical work is against the ambient pressure, the work is $-P dV$), the chemical potential is defined and measured as a ratio of two quantities dE and dN_i that can in principle be measured. For the i th species $\mu_i = (\partial E / \partial N_i)_{S, V, N_j}$. This definition permits writing the fundamental equation as

$$dE = T dS - P dV + \sum_i \mu_i dN_i$$

From this experimentally awkward definition exact relations are derived, some of which serve as alternate, more convenient, and fully equivalent definitions of μ_i (such as *e.g.* the change in Gibbs free energy at constant T and P when the i th species is added), others as bases of methods of convenient measurements and applications. The appearance of the chemical work alongside the engine concepts of work and heat permits a large number of derivations that relate the chemical potential to calorimetric (heat) and equation of state measurements (mechanical work). These relations form the bases of measurement and numerous applications of the chemical potential.

Opening the systems permitted a whole new direction of thermodynamics derivations. For a closed system, the absolute magnitudes of the extensive quantities did not matter; only differential changes were monitored. Gibbs

could start with an empty system and fill it, thereby giving measures for the integral thermodynamic properties of systems. This is especially useful for homogeneous systems; the integral measures can be in turn be differentiated to give the Gibbs-Duhem equation for phases and the Gibbs adsorption equation for surfaces. Gibbs' elegant derivation of the phase rule made use of the Gibbs-Duhem equation.

Adding the chemical work term to the first law equation containing other work terms gives rise to discovering many relations where mobile chemical species interact with physical effects. For example, Gibbs' introduction of the electrochemical potential and the work of moving electrical charge attached to chemical species is the foundation of electrochemistry, electrochemical reactions, and electromigration.

The other work of importance to our field that Gibbs introduced was attached to surface area changes, dA . Its conjugate variable, surface tension σ , is a force per unit length on the perimeter of a piece of fluid surface; σdA is the work of forming or stretching a fluid surface or a fluid film. The definition is based on purely mechanical work, force multiplied by distance, the force on the boundary line of the surface (surface tension times boundary length) times distance the boundary is moved. (Note that dA is the product of boundary length and distance moved.) For fluid surfaces the fundamental equation (with $P dV$ as an example of other work) becomes

$$dE = T dS - P dV + \sum_i \mu_i dN_i + \sigma dA$$

$$\sigma = (\partial E / \partial A)_{S, V, N}.$$

Again Gibbs could start with an empty system, and fill it with a system containing a uniform fluid surface between two uniform phases, thereby getting the integral expressions for σ and upon differentiations, the adsorption equation for how σ changes with changes in T and μ_i . From these manipulations follow predictions of how chemistry, heat, and applied pressure affect the surface tension. Gibbs also treated curved fluid surfaces, set the foundations of homogeneous and heterogeneous nucleation, and derived the conditions for phase equilibria across curved fluid surface.

As an aside, note that, because of these derived relationships, it is of course possible to accomplish much chemical thermodynamics in a closed system with calorimetric heat and equation of state work measurements and to express the thermodynamics of solutions in terms of integral variables, such as the molar Gibbs free energies of mixing. Much of our alloy thermodynamics, and especially modelling is done this way. But vapor pressure and cell potential measurements are still best used as open systems concepts, because they relate to work of adding species to a phase. The appropriate useful open systems free energy is

$$\Omega = E - TS - \sum_i \mu_i N_i.$$

Like the Gibbs free energy, Ω is a minimum at equilibrium, but the conditions under which Ω is minimized are

constant T , V , and all the μ_i . The N_i are allowed to vary. These conditions are realistic and naturally achieved at equilibrium. Fixing the volume is easy; we focus on a fixed sub-volume of the system; a small piece of a phase, an area of surface, etc. The remainder of the system at equilibrium acts as a material and thermal reservoir to fix the μ_i . The advantages are many; among them, there is no need to specify reference state for E and the μ_i because they cancel out; for homogeneous phases $\Omega = -PV$, for surfaces $\Omega = \sigma A$, allowing the equilibrium conditions at curved surface to be expressed entirely in terms of Ω .

These advances and the enormous success of thermodynamics are rooted in these inventions of forms of energy that are more than one hundred years old. Research since then has focussed on well-developed applications, based on rigorously valid relations worked out long ago. Unfortunately this very success has led to a conservative approach, a severe selection of standard problems that are widely used and taught. There is a resistance to tampering with this rigorous and widely applicable field. But the very lesson that the history of thermodynamics tells us is that the first and second law permit inventions of new forms of energy, and that these can lead to new basic developments. I would now like to turn to considerations of solids and surfaces where there appears to be a need for further invention.

III. Diffuse Interfaces

Mechanical work is force multiplied by distance. In an elastic solid, the forces could be the surface tractions, and the distances the surface displacements, both readily measured. But we could equally well look at small volume elements inside the system; then the elastic energy density is an appropriate stress tensor multiplied by well defined strains or displacement gradients.

Gibbs chose to describe surface work by a surface tension or stress multiplied by area increase; both factors are readily measured for fluids. At low powers of microscope observations surfaces look like mathematical surfaces, and area is the proper measure of the quantity of surface. But what if we examine a diffuse interface, between two phases near their critical point, at atomic resolution, or have to deal with nanoscale phases? We would not see a surface, but only a broad region of high gradients in chemistry, structural order or density. What would have been the classical thermodynamics of this subject, if Gibbs had begun with observations on such equilibrated inhomogeneous regions?

Shortly after Hilliard and I began our work on such diffuse interfaces, our colleague Hart⁽⁶⁾ began a highly original fundamental thermodynamic development by defining the gradient content of small volume elements as the important characteristic that describes such systems. Hart showed that it is possible to obtain many of the results of Gibbs' surface thermodynamics from the work of creating the gradients that are in the surface instead of a work of creating surface area. This was a basic thermodynamic development in the spirit of the clas-

sical work. Hart showed that, starting with these quite disparate inventions of work terms, equivalent thermodynamic results can be obtained for planar diffuse surfaces, but his development had new relations pertinent to highly curved surfaces. As is common in the development of basic thermodynamic theorems, there is no need for Hart to linearize. Much of his development does not depend on the assumption of small gradients; making this assumption does give the result that the excess free energy at surface comes from the square of the gradient. Hart's work validated the variational methods that use the square of the gradient in a free energy functionals for equilibria with small gradients, that have been used for many applications, not only for equilibrium, but also for dynamic problems in which surfaces are moving and evolving.

One equilibrium result is a discovery and description of universal perfect wetting near consolute critical points; one of the critical phases almost always prevents contact between any non-critical phase and the other critical phase⁽⁷⁾. This wetting, and the wetting transition⁽⁸⁾ that occurs tens of degrees away from the critical point, have become important subjects of both theory and application. It has led to methods of growing monotectic composites⁽⁹⁾, and to the understanding of non-metallic inclusions in the Fe-S-O system.

Consideration of dynamics is based on partial differential equations that are gradient systems with this free energy as a Lyapunov functional. This is equivalent to defining local thermodynamic potentials as variational derivatives of the free energy. Wherever the derivative with respect to an order parameter, a quantity that is not conserved, is not zero, the order parameter should change locally to lower the free energy. Allen and I showed theoretically that this led to a prediction of motion by curvature of surfaces even though surfaces were not put into the problem, only gradients in the order parameter. Furthermore the theory predicted the surprising result that the velocity of motion would not depend on temperature near the critical point, even though σ would tend to 0, and the thickness of the interface would tend to ∞ . We verified our predictions in Fe-Al and a number of other metallic systems⁽¹⁰⁾.

Crystallinity can be considered an order parameter at diffuse solid-melt interfaces. This is the basic assumption in the development of mathematical methods for studying the kinetics of solidification. Recent computations based on the postulated equations have been able to depict the evolution of dendrites that have many realistic features⁽¹¹⁾⁽¹²⁾.

When the variational derivative of the free energy is with respect to composition, a conserved quantity, gradients in the potential lead to diffusion, giving rise to a modified diffusion equation that has been used to describe spinodal decomposition in which the thermodynamics of the evolution of the surfaces is automatically incorporated⁽¹³⁾. But the methods of thermodynamics allow consideration of all other work terms that might come in. The understanding of the role of magnetic fields

has been a factor in a period of rapid development of permanent magnet alloys. Elastic stresses generated by the diffusion are important, not only in spinodal decomposition, but in the subsequent evolution of microstructure⁽¹⁴⁾⁻⁽¹⁶⁾ and will be discussed in the next section.

IV. Crystalline Solids

In the formative years of thermodynamics in last half of the 19th century, there were many misconceptions about solids. These affected the inventions of work terms, but it is a testimony to the power of classical thermodynamics that much of has survived as our understanding of solids evolved. In the time of Gibbs it was widely accepted that crystals were periodic arrays of identical molecules. Gibbs began the exploration of the consequences of the periodic lattice; this is a topic still being explored. But it was widely accepted that crystals had to obey the law of definite proportion. (Early in the 19th century the law of definite proportions delayed the understanding of fluid solutions as well, but the understanding about solid solutions began much later⁽¹⁷⁾.) The only exceptions to stoichiometric solids treated by Gibbs were solids "which absorb fluids" (moist wood is a good example; Gibbs' development is valid for interstitial carbon in a deformable lattice of immobile iron atoms⁽¹⁸⁾, and with carefully altered definitions can be made valid for all solid solutions⁽¹⁹⁾). Only by dissolving, melting, or vaporizing and then growing with a different compositions could typical solids change their stoichiometry. Even though diffusion in solids was known to craftsmen, scientists seemed to think it impossible, as if part of the definition of a solid, and thus no one looked for it until Roberts-Austen. Solids continued to be mostly ignored well into this century as chemically inert and uninteresting until vaporized, melted or dissolved, and this led to the neglect of their thermodynamics.

A few of the discoveries that altered our views of solids did lead to specific thermodynamic developments. That there are solid solutions is the one that has concerned us most. There is a highly sophisticated and useful thermodynamics of point defects⁽²⁰⁾, but dislocations and their chemical atmospheres have not received equivalent treatment. There is a statistical thermodynamics of ordering that stands apart from classical thermodynamics. Much has been learned about the wide variety of surfaces of, within, and between crystals, but there has only been a case by case thermodynamic development⁽²¹⁾.

The three main attributes of solids that are important for thermodynamics are: their ability to support shear, and thus inhomogeneous stresses; the lattice, which is strictly conserved in many processes and allows only certain discrete variations for others; and the defects, including point defects, dislocations, disclinations, surfaces, interfaces, grain, twin and domain boundaries, stacking faults, etc., that all can be defined precisely through recourse to the lattice. It is convenient to make this an undistorted reference lattice, and make a local mapping

of lattice points into the crystal. This permits the defining of reference volumes, areas, and lengths, and hence, strains and rotations, or displacement gradients. It defines directions and is the cause of anisotropy. It also makes possible the definition of positions in the crystal, to be occupied by atoms or vacancies within unit cell. The lattice is conserved almost everywhere, except at surfaces and some interfaces, where sites can be added or removed, and at dislocations, where sites can be added or removed, and where neighboring sites can move relative to each other.

There are several simple results that illustrate different aspects of the problems posed by the elastic stresses, the lattice, and the defects on the thermodynamics of crystals:

1. Surface area and surface stress

One of the clearest ways in which the lattice affects first law work terms for solid surfaces is that there are two physically distinct ways of changing the area, and more than two for changing the area of an interface between crystals. For fluids there is only one measure of surface area and only one result of changing area reversibly, more of the same surface is created[†]. But for a crystal we can define a surface by identifying points in the crystal with points on a perfect reference lattice, identifying surface points and forming a minimum area surface through these surface points on the lattice. We can define and measure surface area on the lattice in this way; it could be different from the surface area of the actual crystal. An elastic distortion of the crystal, that does not change this mapping, and will not change this surface area in the lattice, even though it might change the surface area of the crystal. There are thus two measures of area that differ by an elastic strain, two independent ways of changing area, two independent work terms, and two independent surface parameters, that could be taken as σ and the surface stress⁽²²⁾. Thermodynamics gives the relationships between them, and also how each is affected by temperature, the μ , and the state of stress⁽²³⁾. The two quantities play different roles in the bending of thin crystals and the increase of solubility or vapor pressure of small crystals, with the related effects on the kinetics of coarsening.

Two of the many kinds of interfaces between solids have been considered thermodynamically. Two crystals with a coherent interface between them can by definition both be mapped onto a single reference lattice. Such interfaces have a σ and a surface stress. Two crystals with an incoherent interface between them are separately mapped onto two reference lattices. This gives not only three descriptions of the interface shape, but also requires a mapping of how the two lattices come together in the bicrystal⁽²⁴⁾. Three work terms seem to be required for simple problems of incoherent equilibrium, but the general formulation is still an open question.

2. Adding atoms to crystals

The process of reversibly stuffing a molecule into a fluid should not depend on where it is placed, because the chemical potentials at equilibrium are constant throughout, even at the surfaces. As a result the fluid volume can grow continuously in mass with a constant chemical potential. This is not so for a crystal; there are a set of ways of adding or removing atoms or molecules from a crystal that result in different states with the same number of atoms, but different lattice specification, different states of strain, and different surface configurations. Let us consider a few of these for simple crystal structures, like body or face centered cubic where atom sites can be identified with lattice points. More complex crystal structures are extensively discussed in large monographs and conference proceedings⁽²⁵⁾:

(1) Remove from or add an atom to a high index large planar surface. Each atom added adds a lattice site, and the volume is increased by the atomic volume in the bulk.

(2) Remove from or add an atom to an edge dislocation along a high index direction. Again each atom added adds a lattice site, and the volume is increased by the atomic volume in the bulk.

(3) Remove an atom from the interior of the crystal in good crystal, away from any dislocation or incoherent surface. The number of atoms is reduced, but the number of lattice sites is constant. A vacancy defect has been created; because of relaxation around the vacancy, the volume of the crystal is not expected to change by an atomic volume. The reverse process is one of stuffing an atom into an existing vacancy.

(4) Stuff an atom into a region of good crystal. The number of atoms increases, but the number of lattice sites does not. An interstitial has been created. (Hillert prefers avoiding the term "interstitial" and calling these atoms on a mostly vacant Wyckoff position.) Again the volume of the crystal is not expected to change by an atomic volume. The reverse process is one of removing an existing interstitial atom.

(5) Continue to place atoms on a low index sharp planar surface, and grow the crystal layer by layer. The average chemical potential is that of process 1 or 2, but during the formation of a single new layer, there will be wide variations, because such a process changes surface topography during the formation of each layer. Gibbs considered the growth of such crystals, and came to the rather disturbing conclusion that the formation of each new layer was a most formidable barrier to crystal growth, and that crystals might not grow when in contact with undercooled or supersaturated fluids. This is an effect of the lattice that was not verified until dislocation free crystals were finally grown⁽²⁶⁾. As predicted from thermodynamics such crystals can coexist with imperceptible (exponential in the reciprocal of the driving force) growth with melts over a range of undercooling or with solutions over a range of supersaturation, in contrast to what the phase rule predicts for equilibria of fluids. If

[†] The exceptions, noted in Gibbs, loc. cit. p. 300, are surfaces of a film thin enough that the interior composition is altered by adsorption to the surface as the film is stretched.

the driving force is high enough such crystals do grow with the rate predicted from a thermodynamic nucleation theory.

(6) Same as (5) but with one or more screw dislocations terminating in the surface. Such crystals are found to grow at rather low driving forces when there are continuing sources of steps on surfaces, such as screw dislocations terminating in the surfaces. Such crystals reach equilibrium with fluids at well defined potentials. Thus the lattice of perfect crystals interferes with the operation of the phase rule, but phase rule equilibrium is accessible for imperfect crystals.

Each of the above is a process of adding or removing atoms with different outcomes. These are open system processes. Closed system processes leave the number of atoms unchanged, but change the lattice.

(7) The first important defect was postulated with closed system outlook; Frenkel considered a process in which both atoms and lattice sites remained unchanged by moving an atom from a lattice site into an interstitial position, always creating equal numbers of vacancies and interstitial defects, an unintentional constraint. A few years later Wagner proposed creating a vacancy in a closed system by putting the atom on the surface, a closed chemical process with an increase in lattice positions.

Let us examine how we get different thermodynamic expressions for the equilibria in a famous example of Gibbs; the homogeneously non-hydrostatic stressed cube composed of a single component. The stress is applied by fluids at three different pressures each in contact with a different pair of opposite faces, P' , P'' , and P''' , that are equal and opposite in sign to the three principal stresses in the cube. Consider growing the cube by adding atomic layers to one of the three faces by process 1. For the energy, entropy, mass, number of lattice sites, and volume change per atom added (V_s) of the solid, the outcome is the same regardless of which face is growing, but the work against the fluids is going to be either $P'V_s$, $P''V_s$ or $P'''V_s$. The work of growing the same homogeneously stressed solid at the three different surfaces differs! Let the fluids be solvents for the solid, which can be equilibrated with three fluids. Thermodynamics can compute the chemical potentials of the dissolved component of the solid in each of the saturated fluids. Gibbs found three different chemical potentials in the saturated solutions in equilibrium with the same homogeneous solid.

$$\mu' = \{(E - TS)/N\}_{\text{solid}} + P'V_s$$

$$\mu'' = \{(E - TS)/N\}_{\text{solid}} + P''V_s$$

$$\mu''' = \{(E - TS)/N\}_{\text{solid}} + P'''V_s$$

In this derivation, the atoms are reversibly exchanged between the solution and surfaces of the solid in contact with that solution; the fluids are not in equilibrium with each other, but each is in equilibrium with the same solid. Note that the three different chemical potentials do not result from the Helmholtz free energy per atom of the solid, which is, of course, the same, but from the

other term, the differences in the PV work per atom when the elements of the solid is added or removed reversibly pushing against the various pressures. The chemical potentials in the fluids converge to a standard Gibbs free energy per atom of solid when the stress is hydrostatic.

Gibbs avoided defining a chemical potential for this homogeneous solid, except in the hydrostatic limit. Note that there is no need to define a chemical potential for this solid in order to find its solubility. Indeed all the usual thermodynamic problems that are solved for fluids using μ , can be solved for solids without defining a μ for the solid. There is a long history of attempts to define a unique scalar μ for a nonhydrostatically stressed solid. Most of these are empty definitions of a quantity with no applications. It is possible to define a chemical potential tensor that reproduces the above equations, but it has meaning only at the surfaces with fluids.

Gibbs went on to point out that all three solutions are supersaturated with respect to precipitating out the hydrostatically stressed solid at that pressure; the driving force is the difference in Helmholtz free energy and is the work of taking the hydrostatically stressed solid and reaching into the fluid with traction forces to change the state of stress of the solid to the nonhydrostatic state while keeping the surrounding hydrostatic.

We can use the above equations to understand some current developments. At small deviations from hydrostatic conditions it seems reasonable to focus on the normal pressure, reasoning that this term is linear in stress, while changes in the Helmholtz free energy are quadratic. But as the Gibbs observation about the supersaturation demonstrates, the change in Helmholtz free energy can be important. In my work with Larché⁽²⁷⁾, we pointed out that any specimen under uniaxial stress is unstable to necking by diffusional creep regardless of whether stress is tensile or compression, even though the normal stress along that surface is constant. This is because the stresses and Helmholtz free energy are higher at the root of the neck and lower at any bump. A number of workers have explored this instability in greater detail, theoretically by Grinfeld, Srolovitz, and Voorhees, and experimentally by Handwerker who all pointed out that stressed surfaces will spontaneously undulate by a variety of diffusive mechanisms.

Since Gibbs did not consider solid solutions, their thermodynamics became an obvious task for Larché and me, and we focussed on an open process of putting in one species (A) on a crystal site and removing an atom of another (B), leaving the lattice unchanged. We found that the work of doing this, M_{AB} was constant at equilibrium, no matter what the phases or their state of stress. If the M_{AB} are not constant, diffusion becomes a spontaneous process; hence the name diffusion potentials for the M . In any fluid $M_{AB} = \mu_A - \mu_B$, and thus we can always find the M if there is any equilibrium fluid. Equations have been derived for how the M change with composition, stress, and temperature, that are quite analogous to those for μ in fluid solutions. The M_{AB} can be generalized to complicated crystal structures with many different

types of Wyckoff sites. The process of exchanging species among sites look very much like chemical reactions, and the thermodynamic treatment of such processes are the basis of much of defect thermodynamics.

The M are defined for lattice defects; for creating a vacancy by process 3 above, it is called M_{vA} . Since in the fluid, μ_A is known and $\mu_v=0$, $M_{vA}=-\mu_A$. For the Gibbs cube there are three different fluids, each with a different μ_A ; thus the M_{vA} can not be constant in such a homogeneous crystal, and be in equilibrium with the A atoms dissolved in the fluid. This equilibrium can now be written in terms of the Helmholtz free energy of the solid and the pressure of the fluid which is the normal pressure exerted on the solid

$$M_{vA} = \{(E-TS)/N_A\}_{\text{solid}} + P_{\text{fluid}} \{V/N_A\}_{\text{solid}}.$$

When the surfaces of a solid experience differing pressures or traction, the M_{vA} at these surfaces will differ (unless there are compensating differences in the Helmholtz free energy), and vacancy diffusion results. If the solid is homogeneously stressed, as in Gibbs cube, the difference in M_{vA} depends entirely on the local normal stresses multiplied by the volume per atom, $P_{\text{fluid}} \{V/N_A\}_{\text{solid}}$. This is the basis of Nabarro-Herring creep by vacancy flow.

In each of these examples for crystalline solids, what happens to the lattice is the important factor that needs to be considered in the chemical thermodynamic development. The reference lattice is important to define the process that is being considered, and the presence and nature of the defects. Within the solid, away from dislocations and surfaces, the lattice sites are conserved quantities, in solids; does it make sense to define a chemical potential of vacancies in fluids? The defects affect diffusion and growth rates and whether a solid can reach global or even local equilibrium.

V. Summary

The history of thermodynamics shows that it provides versatile frameworks for discovery and invention of new relations among quantities that can be precisely defined. If we properly adapt them, the methods can help us deal with our evolving understanding of the idiosyncratic properties of crystalline solids, solid solutions, surfaces, defects, inhomogeneities and structural features on the nanometer scale. Thermodynamics is increasingly featured in non-equilibrium situations, both as inequalities for things that can't happen, and for microstructure evolution equations. The diffuse interface developments have shown that there is an advantage to reexamine with new premises a well established field. Much remains to be done as our understanding of materials evolves.

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