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# The Third Law of Thermodynamics and low temperature phase stability

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## Abstract

The assessment of the low temperature phase stability of alloy phases—substantially below 0 °C—is not only of academic interest but also of considerable practical importance. However, attempts are rarely made to assess phase boundaries as they continue down towards the absolute zero temperature. The purpose of this work is to consider some specific aspects of phase stability, phase boundaries, and the related phase diagrams at low temperatures, in the light of the restrictions imposed by the Third Law we give a brief overview of its place within Thermodynamics. We point out that for ordinary materials the equilibrium state of 0 K simultaneously satisfies the two conditions that its energy and entropy are at their lowest possible values as permitted by the evolutionary constraints imposed on their state variables. Also, free internal state variables (such as the equilibrium compositions of coexisting phases) must be such that the rates of change of their equilibrium values as a function of temperature are zero at 0 K. The phase stability at low temperatures of several binary alloy systems are discussed within the above scheme (Cu–Ni, Cu–Zn, Pu–Ga, In–Sn, Metal–Hydrogen), with the general conclusion that while the Third Law rules out certain configurations of the phase diagram it cannot uniquely determine what the low temperature equilibrium—under the given conditions—must be. For example, the equilibrium state of 0 K of an ordinary crystalline material for which the configurational atomic arrangement is unconstrained, is always perfectly ordered, and the energy of any other configurational state, including the fully disordered state, *must* always be higher. This analysis is particularly important in connection with the long-term aging properties observed in some Pu–Ga alloys.

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## 1. Introduction

Recent compilations of assessed phase diagrams, particularly the binary phase diagrams where Professor Massalski has made special contributions as author and editor [1], have placed specific and increasing emphasis on the fact that all phase diagrams are a consequence of thermodynamics and hence that the experimentally determined, or thermodynamically assessed, phase boundaries must not violate thermodynamic laws, specifically the First and Second Law. This means that the three typical, but different, approaches toward the determinations of a most likely assessed diagram in any system, i.e. through experimental determination of the actual phase boundaries, or by using measured thermodynamic quantities and computations, or via thermodynamic modeling, using carefully assessed parameters, should be all in reasonable agreement. Okamoto and Massalski discussed in detail many reported systems and pointed out that when this is not the case, the proposed boundaries are either thermodynamically impossible, or highly improbable [2].

Another feature of interest is the realization in recent years that the majority of the phase diagrams that have been reported in assessed form are depicted only down to room temperature, or perhaps to 0 °C. This is because below 0 °C the approach to equilibrium may be considered to be effectively frozen (i.e. a state of *constrained equilibrium*) in most systems for practical engineering purposes, and true equilibrium (i.e. *unconstrained equilibrium*) may be unattainable. Hence, only rarely is an attempt made to assess boundaries as they continue towards absolute zero of temperature (hereafter 0 K). Rather, the temperature

range between 0 K and 0 °C is left unexplored, even though in numerous cases the extrapolated trends of many phase boundaries established above 0 °C indicate ranges of solubility at 0 K that appear to be in disagreement with the Third Law of thermodynamics which postulates (as we shall elaborate below) that the entropies of all aspects of a given system reduce to the same value at 0 K, often taken to be zero. From this it follows that random solid solubility is excluded. At the same time, it has been argued [3] that even metastable solid solutions are subject to the Third Law as 0 K is approached.

Another incentive for increased interest in phase diagrams near 0 K is the growing use of computational methods, involving the assessment of phase stability through first principles calculations, which typically yield the ground state energies and phase stability at 0 K. The transition from 0 K to 0 °C must therefore incorporate an understanding of what is happening to the changes in entropy, in particular the entropy related to the transition between the dictated perfect configurational order at 0 K, and the possibility of more relaxed order above.

The interest in the phase boundaries and phase stability between 0 °C and 0 K is not only theoretical. There are several phase diagrams where phase stability considerations substantially below 0 °C are of considerable interest and of practical engineering importance (see for example [4], and Hecker et al. this symposium).

The purpose of the present contribution is to consider some specific aspects of phase stability, phase boundaries, and the related phase diagrams in the light of postulated restrictions imposed by the Third Law of Thermodynamics. Before we discuss specific applications of the Third Law to low temperature phase equilibria we give a brief overview of its place within thermodynamics.

## 2. Laws of Thermodynamics

The First and Second Laws of Thermodynamics are well established. The First Law is essentially a conservation of energy law, positing that the internal energy ( $U$ ) of a system can be increased (or decreased) by either performing work on the system (by the system) or by having heat “flow” into (out of) the system. The First Law shows that both work and heat are forms of energy. It does not say anything about the relationship between “heat” and “work” other than that they both can change the internal energy of a system. The Second Law states that there is a dissymmetry between heat and work. Although all work can be converted to heat, not all heat can be converted to work. The Second Law restricts the possibility of certain processes. In its simplest form it states that the entropy (a thermodynamic parameter that is best defined by the Second Law) of an isolated system always increases until equilibrium is attained. This can be utilized to predict the direction of potential reactions within a system. The Second Law also can be utilized to show that no engine can be built that can convert all the energy due to the input of heat into an equivalent amount of work. There is always a loss or a dissipation of useful energy in the process. These two laws of thermodynamics constitute a solid foundation of physical science as demonstrated by their robustness and longevity.

On the other hand, the Third Law, which was first addressed by Nernst in 1906 [5,6], has been subjected to controversies and disputes [7]. Its usefulness, however, is well established. For example, one of the applications of the Third Law makes possible the *calculation* of high temperature entropies of reaction from calorimetric measurements. Most significant, the calculated values are in agreement with the calculations based on direct *experimental* measurements [8–10].

The mentioned agreement between calculation and experiment fails when metastable or low temperature frozen-in configurations (constrained states<sup>1</sup>) intervene in the calorimetric measurements [10,11]. Therefore, the application of the Third Law might provide a useful tool to decide on the eventual presence of states that are out of equilibrium. In fact, equilibrium and non equilibrium states are important concepts in connection with the Third Law, as we shall emphasize below. Specifically, our interest in this paper refers to the Third Law and its implications for low temperature phase stability.

### 3. Some basic thermodynamic concepts

The application of thermodynamics to the description of the evolution of states (or processes) of a particular piece of matter implies a description of its thermodynamic *state space*. This precedes the specification of its energy and entropy functions in this space, and the particular constraints to which such evolutions may be subjected. All these conditions determine the nature of the possible processes for the system, and completely define the thermodynamic behavior of the particular piece of material under consideration [12–14].

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<sup>1</sup> The concept of constrained equilibrium is important when discussing the application of the Third Law to phase equilibria. The reason for this is that many systems which apparently do not obey the Third Law are in a state of *constrained equilibrium*. What do we mean by this concept? Consider a system whose internal energy ( $U$ ) and entropy ( $S$ ) can be written as:

$$U = U(V, S, N_i, \eta_i)$$

$$S = S(V, U, N_i, \eta_i)$$

where  $N_i$  are the composition variables and  $\eta_i$  are any other thermodynamic state variables that play a role in determining the equilibrium state of the system (e.g. magnetization, atomic order parameter, etc.). For a “full” or *true* equilibrium the system must attain equilibrium with respect to *all* of its state variables. If one of the variables (say  $\eta_3$ ) is constrained to have a fixed value other than its equilibrium one, the equilibrium that is attained by the system is called a *constrained equilibrium*.

Suppose for example that the phases present in a system are not able to change their composition below a certain temperature. Thus, the final state of the system will in principle not be the true equilibrium state of the system. The (partial) equilibrium that is attained however is a *constrained* one and if diffusion is allowed (perhaps by an influx of vacancies) we expect that the system will finally obtain its true equilibrium with respect to the values of the composition of the phases.

Chemical composition is an important variable in connection with phase diagrams. Its conjugate force for each component is the corresponding chemical potential  $\mu$ , and composition changes can be thought to be imposed on the material by a reversible matter reservoir of variable  $\mu$  [12,13].

We presume that for the materials considered here all reasonable continuity requirements and good mathematical behavior are met by the corresponding thermodynamic functions in the state space. For the materials of interest, it is always the case that their absolute temperature  $T$  can be equal to or greater than 0 K and the temperature can take any positive value up to infinity ( $T \geq 0$ ). Intrinsic *stability inequalities* are all always assumed to be valid; *constraints* represent well the particular conditions of the evolution of the material system; and, loosely speaking, “maximum entropy” and “minimum energy” are equivalent criteria able to determine any of the equilibrium states for positive  $T$  [14].

We note that thermodynamics does not depend upon nor does it compel, the acceptance of any specific model of matter. However, the fact that the mechanical conserved quantities of internal energy ( $U$ ), momentum ( $\mathbf{P}$ ), and angular momentum ( $\mathbf{L}$ ) can be defined for any state of any material system is in accordance with the successful description of matter which has been done by means of models based on (statistical) mechanics [15].

Mechanical systems are those systems which can be completely described by the Laws of Mechanics (classical or quantum) [16]. Processes in these mechanical systems are always reversible and conditioned only by the conserved mechanical quantities and the acting constraints. Since entropy is essentially related to irreversibility, it does not participate in the analysis of the time evolution of mechanical states. For this reason it is possible to establish that the entropy of *any* mechanical state is equal to zero.<sup>2</sup>

Let us now take a closer look at the specification of material states, that is, at the corresponding thermodynamic state space. It appears that, for those materials involved in everyday life as well as in all kind of engineering applications, states are in fact quite complex. To specify these states properly a large number of state variables would generally be needed.

Dynamically, and in connection with the modeling of a particular process, state variables may be classified in frozen and free variables. This classification depends on the process of interest and the type of modeling required. Frozen variables are taken to be strictly constant during the process and free variables are assumed to evolve fast enough to be able to reach the equilibrium value compatible with all imposed constraints.

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<sup>2</sup> This assignment of zero entropy to any mechanical state is the usual practice in the applications of Thermodynamics. This convention is also applied when Thermodynamics is modeled by means of Statistical Mechanics [16]. If the assignment of zero entropy to any mechanical state were not the case, (which is possible) then the entropy of mechanical states should be explicitly included when considering the total entropy change of an evolving system containing a mechanical subsystem. In addition, mechanical states can then have their own absolute temperature  $T_{\text{mech}}$ . In the usual practice of adopting  $S(\text{any mechanical state})=0$ ,  $T_{\text{mech}}=\infty$ . Whatever value of  $T_{\text{mech}}$  may result, all mechanical states should have the same absolute temperature  $T_{\text{mech}}$ . Besides, if  $T_{\text{mech}}$  were positive, then the absolute temperature of any given piece of material would not be able to become higher than  $T_{\text{mech}}$  because normal friction processes must be irreversible. The modification of the condition  $S(\text{any mechanical state})=0$ , however trivial it might look, would have consequences that can not be dismissed.

It is also common to classify state variables as either external or internal in the sense that they are either externally-controllable or uncontrollable [17,18]. Internal variables can be measured but they are not under external control in the system under consideration. Both external and internal variables can be either frozen or free, depending on the way in which the evolution of the system takes place, or is being modeled. Order parameters [15] are, in general sense, free internal variables.<sup>3</sup>

### 3.1. General thermodynamic behavior of materials at low temperatures

The following discussion is based on the entropy representation [14,19,20]. The states of a given material are assumed to be correctly specified by a necessary and sufficient set of scalar state variables:  $U$ ,  $N$ ,  $V$ , and  $\eta$ . In this set,  $U$  is the internal energy,  $N$  denotes the compositional variables ( $N_j$  with  $j=1, 2, 3, \dots$ ),  $V$  is the volume and  $\eta$  denotes collectively the remaining state variables, appropriately defined for the purposes at hand;  $\eta \equiv \eta_1, \eta_2, \eta_3 \dots$ . Thus, the full description of the thermodynamic behavior of a given material is established through an entropic fundamental relation of the form:

$$S = S(U, N, V, \eta).$$

In what follows, for brevity, a particular state  $U$ ,  $N$ ,  $V$ ,  $\eta$  will be denoted generically by  $Z$ ; that is  $Z \equiv U, N, V, \eta$ , and  $S = S(Z)$ .

We assume that  $S = S(Z)$  is analytic in each of the variables and therefore differentiable and continuous to all orders within the range of the values of  $Z$  admissible for the given system.<sup>4</sup>

One of the important conclusions of the mechanical microscopic model of the thermodynamic properties of matter, as provided by statistical mechanics, is that *for any state  $Z$  there exists a mechanical state  $M$  such that  $M$  can evolve spontaneously and in isolation to  $Z$  [9,12,16,21,22].*

Since, as remarked above, the entropy of any mechanical state must be taken to be zero, such a basic conclusion implies that a positively defined entropy function  $S = S(Z)$  exists. That is:

$$S = S(Z) \geq 0 \text{ for any } Z.$$

This “absolute entropy” function is uniquely defined over all states  $Z$  up to a positive multiplying constant, a gauge which maintains invariable the condition  $S(\text{any mechanical state}) = 0$ .

<sup>3</sup> Examples of internal state variables are: configurational atomic order, microstructure, pair distributions, isotope distributions, defects of all kinds and their distributions, inhomogeneities and gradients. Examples of external or internal state variables, depending on the system arrangement, are: crystal structure, volume, electrical and magnetic polarizations, local strains and chemical composition.

<sup>4</sup> This means that the physical situation at 0 K coincides with the result of taking the limit as  $T \rightarrow 0$  K.

We will now explore some of the properties of the absolute entropy of a system in the state  $Z$ , at and near  $T=0$  K. For convenience we will consider all thermodynamic extensive state variables such as  $S, U, V$  as divided by  $(\sum N_j)$ .

We start our analysis with all the thermodynamic state variables fixed except for the internal energy  $u = U/(\sum N_j)$  and the volume  $v = V/(\sum N_j)$ .

We may then plot the equilibrium surface of the entropy ( $s$ ) as a function of internal energy ( $u$ ) and volume ( $v$ ). In this case,  $s = s(u, v)$ . The equilibrium state obtained from an iso-energy section is the same as that obtained from an isoentropic section. The minimum in energy at constant entropy corresponds to a maximum in entropy at constant energy for the same equilibrium value of the volume. This is an illustration of the equivalence of the maximum entropy and minimum energy principles [14,23]. The slope of the constant energy curve becomes infinite when the temperature is zero since:

$$\left(\frac{\partial s}{\partial v}\right)_u = \frac{P}{T}.$$

Fig. 1 shows a plot of  $s$  versus  $u$ , in which  $v$  together with all the other thermodynamic parameters such as  $\eta$  are held constant. There are several important features to be pointed out.

First, the slope of the plot at any point has a value of  $1/T > 0$  and the curvature of the plot is:

$$\left(\frac{\partial^2 s}{\partial u^2}\right)_\eta = -\frac{1}{T^2} \left(\frac{\partial T}{\partial u}\right)_\eta = -\frac{1}{T^2 C_\eta}.$$

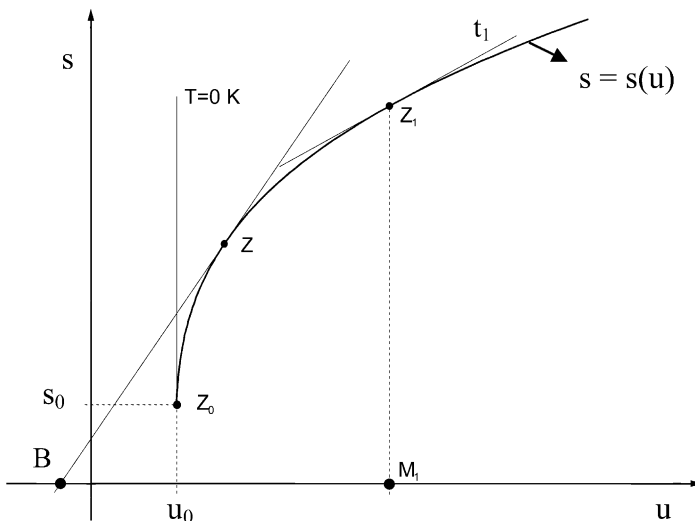


Fig. 1. An entropy versus internal energy plot of a material, holding the volume and all other  $\eta_i$  constant. The slope of the curve equals the reciprocal of the absolute temperature.

Since heat capacities must be positive for intrinsic stability [14], the curvature must be negative everywhere.

Another thing to note about Fig. 1 is that the intersection of a tangent to the curve (at B for example) is the value of the free energy at the temperature represented by the slope of the tangent. When the tangent approaches a vertical (at  $Z_0$ ) the temperature approaches 0 and the free energy becomes identical to the internal energy  $u_0$ . The point represented by  $Z_0$  shows that there must be a minimum value of energy (the ground state energy  $u_0$  for constant  $\eta$ ) at  $T=0$ , as well as a minimum value of the entropy ( $s_0$ ).

A final thing to notice in Fig. 1 is that a system can evolve from a zero entropy mechanical state  $M_1$  to its final equilibrium state  $Z_1$  of positive entropy. As mentioned above, all possible thermodynamic states have absolute entropies greater than or equal to zero.

Fig. 2 is a plot similar to that of Fig. 1 but in this plot the  $s$  versus  $u$  curves are shown for several values of the internal thermodynamic parameter  $\eta$ . The solid curve is the upper envelope of the curves and represents the equilibrium states of the system with respect to  $\eta$ . This corresponds really to a projection of the surface  $s(u, \eta)$  onto the  $s/u$  plane. For each of the values of  $\eta$  it can be seen that there are endpoints of the curve for  $T=0$ , with different values of  $s_0(\eta_i)$  and  $u_0(\eta_i)$ . Of course the equilibrium state at  $T=0$  K is the one with the minimum energy  $u_0(\eta_i)$ . Whether or not

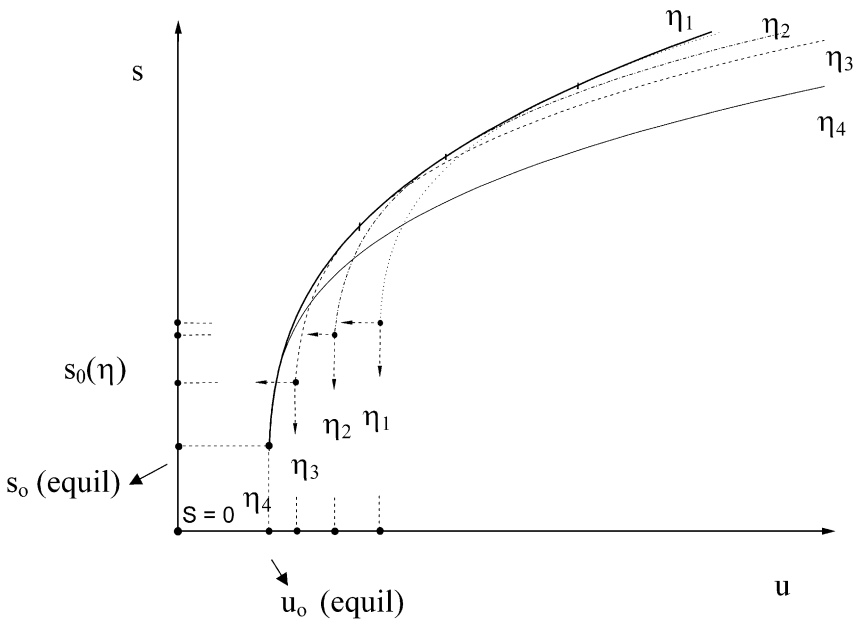


Fig. 2. An entropy versus internal energy plot of a material holding the volume constant but allowing the internal thermodynamic parameter  $\eta_i$  to vary. The upper envelope of the curves defines the equilibrium states of the material.



the  $T=0$  states for different values of  $\eta$  really have different values of entropy is a matter to be discussed later. For now we allow in principle for different values.

In 1906 Nernst noticed that the differences in several of the auxiliary thermodynamic functions approached zero as the temperature approached zero [5,6,14,24,25]. From this he based his initial statement of the Third Law, namely that at  $T=0$  K all substances in equilibrium have the same value of entropy. In this paper we call this the Nernst statement of the Third Law. Some time later Planck noted that this value of entropy could be set equal to zero with no loss in generality [26].<sup>5</sup>

Later, in 1917, Nernst also stated a related law which following Callen [14] is expressed as “...no reversible adiabatic process starting at (a positive) non-zero temperature can possibly bring a system to zero temperature”. This is known as the unattainability statement of the Third Law [3,9].

There has been much discussion in the literature of whether one of these statements implies the other and vice versa. In what follows we will discuss further aspects of the Third Law, including the relationship between the two statements.

As we mentioned above, the entropy at 0 K can in principle have different values as a function of the free parameter  $\eta$  (see Fig. 2). However, experimental information available on the behavior of most materials (called *ordinary materials* in this paper) shows that the dependence of  $s_0$  on  $\eta$  is restricted. This can be seen by considering the rate of change of the equilibrium value of  $\eta$  as a function of temperature at 0 K. The general thermodynamic expression:

$$\frac{\partial \eta_{\text{eq}}}{\partial T} = \frac{\left(\frac{\partial s}{\partial \eta}\right)_T}{\left(\frac{\partial^2 f}{\partial \eta^2}\right)_T} \quad (1)$$

(derived from the equilibrium condition  $\left(\frac{\partial f}{\partial \eta}\right)_T = 0$ ) establishes the direct proportionality between  $\frac{\partial \eta_{\text{eq}}}{\partial T}$  and  $\left(\frac{\partial s}{\partial \eta}\right)_T$ . Since experimentally ordinary materials show  $\left(\frac{\partial \eta_{\text{eq}}}{\partial T}\right)_{T=0} = 0$ , it is natural to conclude that  $\left(\frac{\partial s}{\partial \eta}\right)_{T=0} = 0$  as well. This is an important conclusion.

For thermodynamic state variables  $\eta$  that have conjugate forces (that is, they are variables that can be reversibly controlled by an external force, which includes volume, magnetization, electric polarization and chemical composition) this implies that at 0 K the entropy of the materials system is independent of the value of  $\eta$ .

<sup>5</sup> This can be seen as follows: suppose at 0 K a crystalline phase of one component (i.e. an element) is in equilibrium with another crystalline phase which is made up of two components, i.e. an alloy. The one component crystalline phase has no configurational entropy at 0 K and since it is in equilibrium with the two component phase that phase must also have zero configurational entropy, which means it must be a stoichiometric perfectly ordered phase. Other possible contributions to entropy coming from ignored or even unknown internal degrees of freedom are irrelevant to the obtained equilibrium state. Hence the entropies of both phases can be set equal to zero with no loss of generality.

Consequently for this case the  $T=0$  isotherm coincides with an isentropic curve on the entropy surface which confirms the Nernst statement of the Third Law (see Fig. 3). Fig. 3 shows the surface of the entropy function that is consistent with the discussion just made.

This explanation gives a solid experimental basis to both the Nernst and the unattainability statements of the Third Law as stated above. It is clear from Fig. 3 that if a system starts at a positive temperature (e.g. point A) and energy is removed from it at constant entropy, equilibrium is attained at point B where a minimum in energy and then a maximum in entropy obtains. This isentropic curve which passes through points A and B will never cross the  $T=0$  isotherm. Hence, the unattainability statement according to Callen [14] holds for this general behavior of the entropy. Thus, Fig. 3 represents both statements of the Third Law as given above.

For some systems it is well known that the entropy at 0 K has a residual positive value with respect to the true equilibrium state at 0 K [3,25]. This arises because the system is constrained to be in a state that at  $T=0$  K is out of equilibrium. This is the case for glasses, quenched disordered alloys, solid CO, etc. This is a consequence of the constraints acting on the system and not allowing the internal state variables to relax to their equilibrium values. This situation can be rationalized by considering Fig. 4. The  $T=0$  isotherm is seen to rise in entropy at all points away from the equilibrium state where the entropy is in fact at a minimum together with the minimum in energy. While the condition shown in Fig. 4 may be consistent with the unattainability statement (the system can not decrease its energy at constant entropy

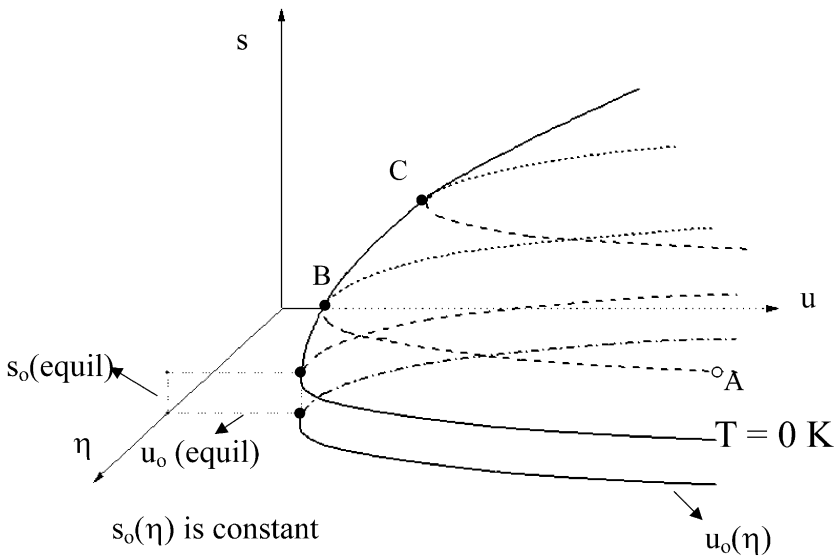


Fig. 3. An entropy, internal energy and  $\eta_i$  surface of a material consistent with both the unattainability statement of the Third Law and the Nernst Statement of the Third Law. Note that the isotherm  $T=0$  is also isentropic.

and reach the equilibrium state at 0 K) it is not consistent with the Nernst statement of the Third Law.<sup>6</sup>

Fig. 5 shows a case which is inconsistent with both statements of the Third Law, that is, the entropy is not a minimum at equilibrium nor is the unattainability principle valid. However, the entropy surface is not incompatible with the unrestricted application of the first and second laws of thermodynamics, and so it is possible that it may represent rather unusual materials which have not as yet been found or investigated [27].

#### 4. Applications to low temperature equilibria

In this section we provide several examples of the application of our understanding of the Third Law of Thermodynamics to specific binary alloy systems. When applying this Law to low temperature phase equilibria, we will see that the Law may rule out certain configurations of the phase diagram but that it cannot uniquely determine what the low temperature equilibrium must be. This is because the Law merely states that at 0 K the equilibrium state should have its lowest entropy: it does not state unequivocally in what way the system must configure itself to obtain this entropy. Thus, an alloy of composition 50%B in an AB system at 0 K, where the atomic spatial configuration is unconstrained, may either atomically order or decompose into the two elements of which it is composed in order to obtain minimum entropy, depending on the corresponding enthalpy value of the alloy [28].

<sup>6</sup> Let us consider an ordinary material system whose thermodynamic behavior is described by

$$S = S(U, V, \eta)$$

where all other possible state variables of the system are not explicitly stated and are taken to be frozen—kept fixed—or fully relaxed. Thus, at 0 K, the entropy is

$$S_0 = S_0(V, \eta) = S(T = 0, V, \eta).$$

Now, from the stated properties of  $S_0$  for ordinary materials, if  $S_0$  is considered as a function of the volume  $V$  for any given value of  $\eta$ , results

$$(\partial S_0 / \partial v)_\eta = 0, \text{ for every } \eta.$$

Therefore,  $S_0$  reduces to be only a function of  $\eta$ :  $S_0(V, \eta) \equiv S_0(\eta)$ .

Accordingly, for ordinary materials we have that either

- $S_0(\eta)$  has only one or more isolated minima at certain specific values of  $\eta$
- or
- $S_0(\eta) = \text{constant}$ , for all values of  $\eta$ .

The former is the case when, for example,  $\eta$  represents a configurational parameter, such that a minimum occurs at well defined and different types of perfectly ordered spatial (crystalline) arrangements. A maximum in  $S_0(\eta)$  necessarily represents an unstable state at 0 K, as will be the case of an ideal disordered solid solution.

In the second case,  $S_0$  remains strictly constant as a function of both state variables,  $\eta$  and  $V$ ; that is  $S_0(V, \eta) = \text{constant}$ , in coincidence with the Nernst statement of the Third Law.

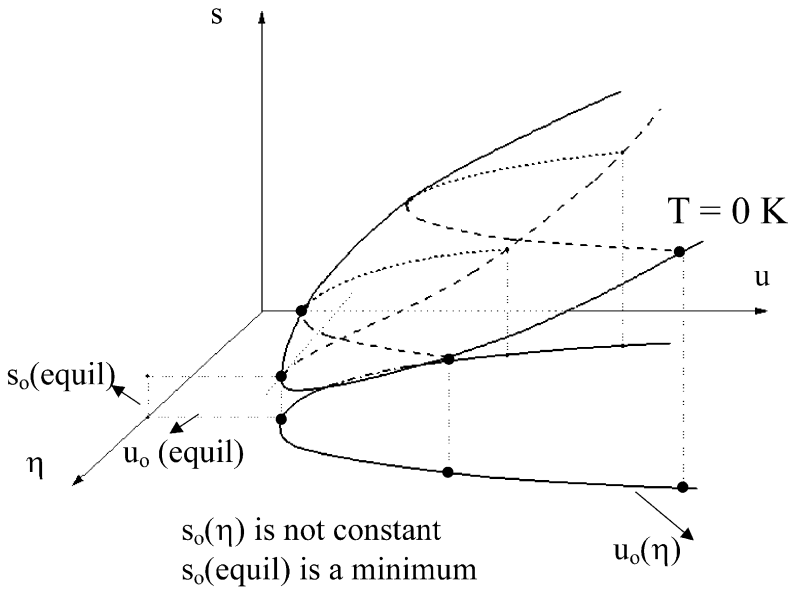


Fig. 4. An entropy, internal energy and  $\eta_i$  surface of a material, which is consistent with the unattainability statement of the Third Law but not with the Nernst Statement of the Third Law.

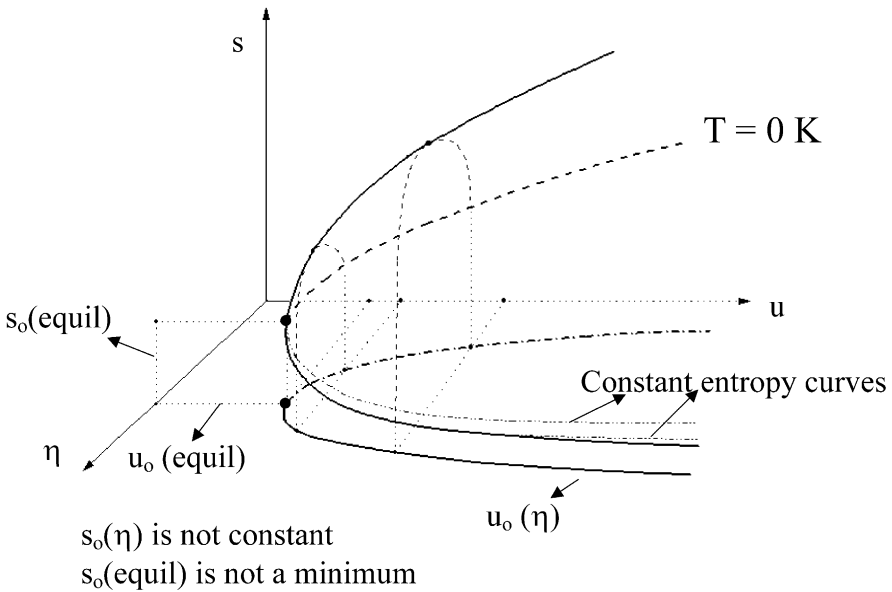


Fig. 5. An entropy, internal energy and  $\eta_i$  surface of a material, which is inconsistent with both the unattainability statement of the Third Law and the Nernst Statement of the Third Law.

Also, the specific ordered phase to which it may transform cannot be determined by entropy considerations but rather by enthalpy considerations on the alloy system.

#### 4.1. Copper–nickel system

The continuous fcc solid solution between Cu and Ni is often cited as an example of a nearly ideal solid solution. No intermediate or ordered phases were reported in this system in the early phase diagram compilations [29]. However, the ideal solid solution behavior does not conform to the Third Law requirements when extrapolated to equilibrium states down to 0 K. This has been experimentally confirmed by the clustering tendencies observed in Cu–Ni alloys at temperatures below 100 °C, including evidence of cluster growth at room temperature in alloys close to 50 at.% [30]. Much indirect experimental evidence based on changes of the physical properties such as the electrical resistivity, the Hall coefficient, magnetic clustering, neutron small-angle scattering, and electron microscopy [30] have demonstrated that there exist tendencies in Cu–Ni alloys to decompose into the Cu enriched and Ni enriched fcc regions.

These experimental observations support the hypothesis that a miscibility gap between pure Cu and pure Ni develops in the Cu–Ni fcc solid solution at low temperatures, in agreement with the entropy requirements of the Third Law. However, direct confirmation of this miscibility gap (that is the actual observation of the two phase equilibrium) has not been possible due to the extremely slow kinetics of the decomposition process.

The currently accepted phase diagram for the Cu–Ni system, which satisfies the Third Law, is shown in Fig. 6. Included in the diagram is the magnetic transition in Ni. Thus the two phases in equilibrium at 0 K are predicted to be Cu and ferromagnetic Ni.

#### 4.2. Copper–zinc system

The phase boundaries of the Cu–Zn phase diagram are accurately known experimentally to 200 °C [31]. It is remarkable that the solubility limit of Zn in the fcc phase of Cu, represented by the  $\alpha/(\alpha + \beta)$  boundary shown in Fig. 7, extrapolates at room temperature to a composition close to 30 at.% Zn. This is a rather large primary solid solubility at room temperature, and in principle can be considered as incompatible with the entropy demand imposed by the Third Law on the equilibrium states of the alloy at 0 K. However, a potential configurational ordering of the  $\alpha$  phase in the 25 atomic percent region has been detected experimentally at temperatures as low as 100 °C, where neutron diffraction, electrical resistance and thermoelectric power measurements, together with calorimetric results [31] show anomalies which suggest that atomic rearrangements are taking place in the fcc structure of the  $\alpha$  phase. Such low temperature rearrangements are manifestations that the alloy is attempting to change its state in order to conform with the Third Law requirement of minimum entropy at 0 K. That is, either the  $\alpha$  phase will order atomically, or it will decompose into two coexisting ordered phases (or an ordered phase and pure Cu), upon reaching equilibrium at 0 K.

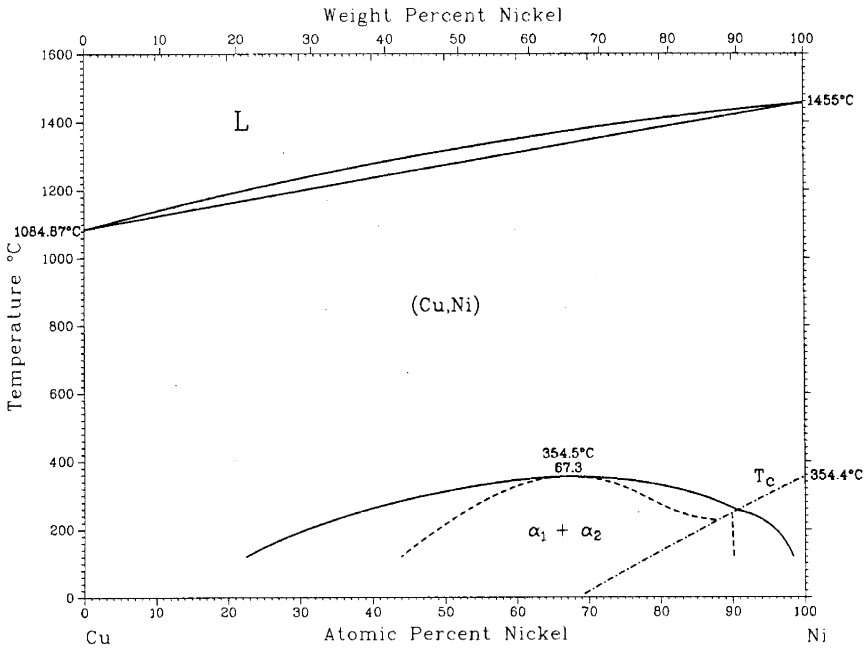


Fig. 6. The Cu–Ni phase diagram from Ref. [30].

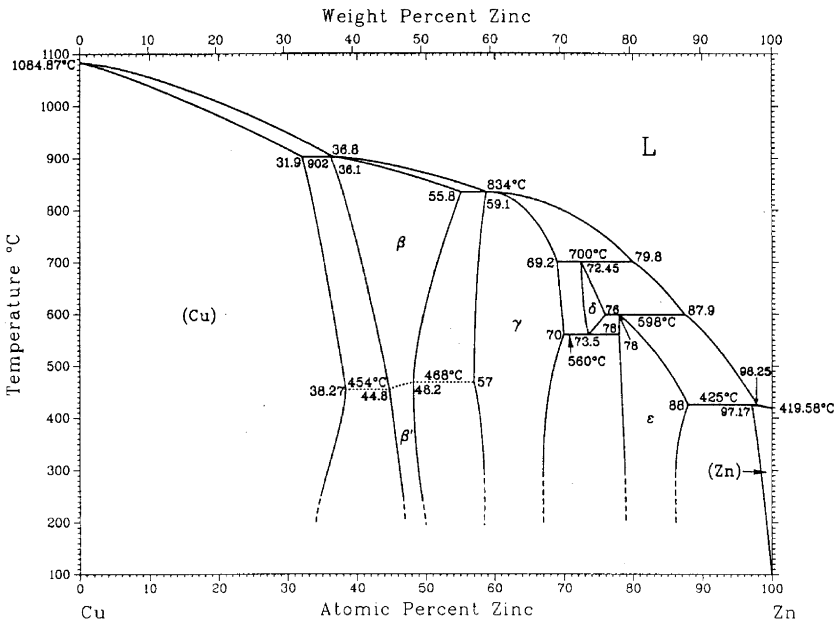


Fig. 7. The Cu–Zn phase diagram from Ref. [31].

In view of the foregoing discussion and of the little dispute existing about the high temperature phase boundaries of the Cu–Zn system, the elucidation of the true equilibrium phase diagram close to 0 K remains an interesting question. In this connection, a simple guess would be a monotectoid decomposition of the  $\alpha$  phase, namely,  $\alpha \leftrightarrow \alpha\beta'$ , at or below about room temperature.

The  $\beta'$  phase boundaries could come together at 50 at.o Zn at 0 K to satisfy the third law. Also the disordered phases  $\gamma$  and  $\epsilon$  could either atomically order or decompose into phases which are capable of obtaining zero entropy at 0 K.

#### 4.3. Plutonium–gallium system

The Pu–Ga system has been extensively studied in the composition range near 5 at.% Ga, where the high temperature fcc- $\delta$  phase of Pu becomes the stable phase at temperatures close to room temperature and below. However, two qualitatively different experimental phase diagrams at low temperatures have been reported for the Pu–Ga system. These diagrams are shown in Fig. 8.

The first diagram (Fig. 8a) shows the existence at low temperatures of an extended range of solubility of Ga in  $\delta$ -Pu, from 2 to 8 at.% Ga, essentially in the form of a substitutional disordered solid solution (Fig. 8a) [32,33]. This disordered state can only be obtained under the constraint of frozen configurational parameters for the alloy. Such a case may arise if, for example, diffusion by the vacancy mechanism is the only possible way for the evolution of the alloy to proceed, and if the vacancies are not able to move. However, if other mechanisms of change are possible, being triggered for example by alpha decay, the fcc- $\delta$  phase may be subjected to change and the unconstrained configurational equilibrium state may be approached. Of course, considering Pu–Ga to be an ordinary material, the Third Law prescribes that the configurational parameters will evolve with time finally to reach a state of equilibrium at 0 K at the lowest possible energy and entropy. Thus, by reason of the Third Law, at 0 K the fcc- $\delta$  phase probably phase separates into a coexisting pure Pu and an ordered phase, constituting the final equilibrium state.

Other authors (Fig. 8b) [34] do show experimental results that indicate a two phase field ( $\alpha$ Pu<sub>3</sub>Ga) at low temperatures as the stable equilibrium state. Disregarding isotope effects, these results are consistent with the Third Law. However, since these experimental results were obtained by initially seeding the sample with one of the precipitating phases [34,35] this in fact may define a constraint on the system, and therefore a doubt still remains regarding the true character of the final equilibrium that might be detected experimentally. This last comment is not merely of an academic nature, but is indeed important from the materials engineering point of view in terms of the aging properties of Pu–Ga alloys. Further experimental research to clarify this point is certainly of interest.

#### 4.4. Indium–tin system

The In–Sn phase diagram is shown in Fig. 9 [1]. Here again the phase field of the disordered  $\gamma$  phase (hP1) appears to be stable to 0 K with a solubility range of

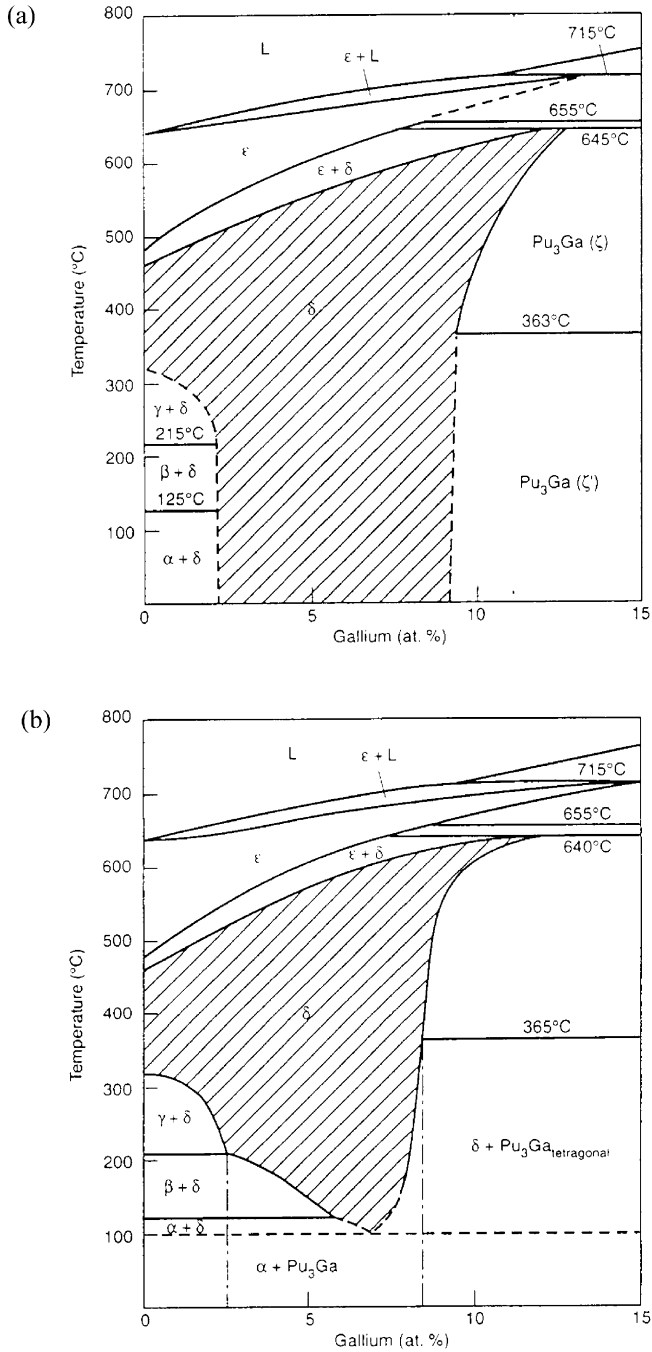


Fig. 8. Two different proposed phase diagrams of Pu–Ga given in [4].



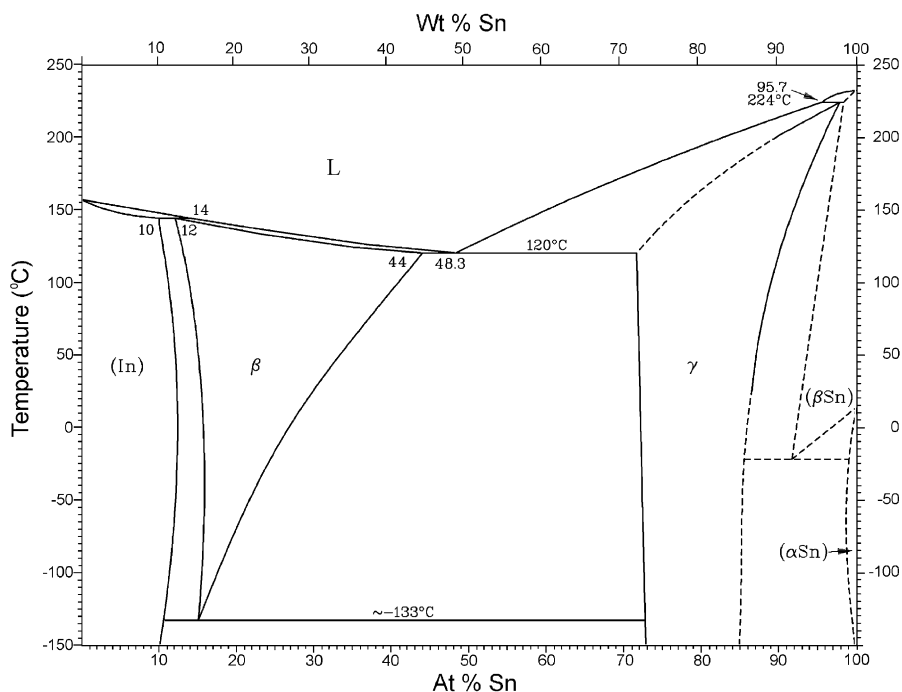


Fig. 9. Phase diagram of the In–Sn system [1].

73 to 81 a/o Sn. Clearly, this is unlikely and we are currently investigating the low temperature stability of this phase [36]. We believe that the  $\gamma$  phase is likely to decompose into In (tI2) and Sn (diamond structure, cF8) at low temperatures. The fact that the In-rich (tI2)  $\beta$  phase has been observed to decompose at 140 K gives us some expectation that such a transformation is kinetically possible also on the Sn rich side of the diagram. Of course there are other scenarios possible for the phase diagram of InSn that would be consistent with our presentation of the Third Law. For example, the  $\gamma$  phase could order at low temperatures and the solubility range would be close to zero at 0 K. In any case, the large configurational entropy of the  $\gamma$  phase dictated by the diagram shown in Fig. 9 makes this diagram unlikely.

#### 4.5. Palladium–hydrogen and some other metal–hydrogen systems

Metal–hydrogen systems are particularly interesting for the purposes of the present discussion because their diffusion and structural kinetics are still significant at temperatures well below room temperature [37]. Thus, low temperature features of the corresponding equilibrium phase diagrams are in principle more readily accessible experimentally than in the case of other solid solutions.

Metal–hydrogen systems would be specially appropriate for investigating experimentally the temperature dependence of the equilibrium composition values  $x_\alpha$  and

$x_\beta$  of two coexisting phases,  $\alpha$  and  $\beta$ , as  $T$  approaches 0 K. According to our discussion above, the internal state variables (the compositions  $x_\alpha$  and  $x_\beta$ ) must certainly satisfy an expression of the form given in Eq. (1). This expression is related to the well known Gibbs–Kononov formula [7,16, 38] which, evaluated at  $T=0$  K, yields

$$\left(\frac{\partial x_\beta}{\partial T}\right)_{\text{equil}; T=0} = \frac{\Delta S_0(\text{for the precipitation of } \alpha \text{ in } \beta)}{\left(\frac{\partial^2 h^\beta}{\partial x_\beta^2}\right)_{\text{equilibrium}} (x_\alpha - x_\beta)}. \quad (2)$$

This last equation is of course a particular case of the general expression given in Eq. (1) which led to the conclusion that  $\left(\frac{\partial s}{\partial \eta}\right)_{T=0} = 0$ . The Third Law requires that

$$\Delta S_0(\text{precipitation of } \alpha \text{ in } \beta) = 0$$

$$\text{Thus we obtain, as expected, } \left(\frac{\partial x_\beta}{\partial T}\right)_{\text{equil}; T=0} = 0.$$

$$\text{Similarly, for } x_\alpha \text{ this is } \left(\frac{\partial x_\alpha}{\partial T}\right)_{\text{equil}; T=0} = 0.$$

Therefore, as a result of the Third Law, the equilibrium boundary lines at 0 K should be vertical in the usual temperature–composition phase diagrams of ordinary materials. This is a completely general conclusion.

There is indeed a considerable amount of experimental evidence available that indicates that phase boundaries in metal–hydrogen systems are vertical in temperature–composition diagrams as  $T$  tends to 0 K, confirming the prescription dictated by the Third Law. This statement can be compared with the several examples given by Manchester in [37]. These examples include the low temperature miscibility gap in the fcc phase of the Pd–H alloy, the  $\alpha + \beta/\beta$  boundaries in the V–H and D–V phase diagrams, and the  $\alpha + \epsilon/\epsilon$  phase boundary in Nb–H.

A further observation on the experimental phase diagrams data given by Manchester [37] for several metal–hydrogen systems, is the definitive existence of a tendency of alloys to atomically order at low temperatures, close to 0 K. This is in full agreement with the requirements of configurational ordering in terms of the Third Law, as already discussed for example in the case of the Pu–Ga system.

## 5. Concluding comments

For an ordinary material the equilibrium state at 0 K simultaneously satisfies the two conditions:

1. The energy of the material is at its lowest possible value; and
2. The entropy of the material is at its lowest possible value.

Therefore the following holds:

1. The structure of the equilibrium state of an ordinary material at 0 K, when the atomic spatial positions are unconstrained, will always be crystalline. This agrees with the observed exothermal crystallization of noncrystalline amorphous materials and with the nonzero positive entropy associated with the noncrystalline amorphous state.
2. The equilibrium state at 0 K of an ordinary crystalline material for which the configurational atomic arrangement on a lattice is unconstrained, is always perfectly ordered, and the energy of any other configurational state, including the fully disordered state, must always be higher. Thus, the equilibrium state at 0 K of an ordinary material in its crystalline state which is under no constraints with respect to atomic rearrangement, will always involve phases which are either pure, or which are fully atomically ordered. The equilibrium state at 0 K of an ordinary crystalline material for which the configurational atomic arrangement is unconstrained, cannot be correctly represented by the ideal solution model because, in such a case, its configurational entropy would be a maximum and not a minimum as required by the Third law.
3. No reversible adiabatic process starting at nonzero temperature can possibly bring an ordinary material system into its equilibrium state at 0 K. This is so because the equilibrium state has the lowest possible entropy.
4. Since the volume of the equilibrium state at 0 K of an ordinary material system can attain any of its allowed values, depending on the applied external pressure, the entropy at 0 K for this material will be independent of volume (or pressure). This is because the purely mechanical, external forces, producing the pressure, do not contribute to the total entropy.
5. More generally, since the (volume, strain, electric and magnetic polarizations and chemical composition) of the equilibrium state of an ordinary material at 0 K can attain any of its allowed values, depending on the externally applied fields (pressure, tension, electric, magnetic and chemical potentials), the entropy at 0 K will be independent of (volume, strains, polarizations, composition) (or pressure, tensions, fields, chemical potentials).

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