Chapter 7: The Third Law

7.1 INTRODUCTION

The Third Law of Thermodynamics gathers several important observations on the behavior of systems at very low temperature into a single general rule. The observations include the following.

1. The most striking outcome of low-temperature experiments is the failure to achieve the absolute zero of temperature. While low-temperature physicists are constantly setting new records for minimum temperature, each order-of-magnitude decrease has required a commensurably greater experimental effort. The results suggest that temperature asymptotes toward zero without actually reaching it. This conclusion is not inconsistent with the Second Law since the requirement that T not be negative is satisfied if T only exists in the open interval T > 0.

2. The values of the thermodynamic properties of real materials show a surprising uniformity as temperature approaches zero. The specific heats of all known substances vanish as T → 0 to an order that is at least linear in T; the specific heat of a metal is proportional to T near T = 0 while that of an insulator or semiconductor is proportional to T^3. The coefficient of thermal expansion of a solid and the variation of its pressure with temperature vanish as T → 0 along with a number of other material properties. In fact, if q and p are a geometric coordinate and its conjugate force, it is always found that

$$\frac{\partial p}{\partial T} \bigg|_q = \frac{\partial q}{\partial T} \bigg|_p = 0 \quad 7.1$$

where the subscripts indicate that the partial derivatives are taken with q and p, respectively, held constant.

3. All known substances seek minimum-entropy states as the temperature approaches zero. Fluid phases condense into crystalline solids and solid solutions order or decompose into ordered phases.
4. The entropy changes in standard chemical reactions vanish as $T \to 0$ as do the entropy differences between different crystalline modifications of the same substance. The entropy differences between the simple states of pure components and other states that have frozen-in degrees of freedom, such as a crystal and a glass of the same substance, do not vanish as $T \to 0$, but tend toward small, constant values. In many cases these small differences can be calculated from statistical thermodynamics, and prove to be just the difference in configurational entropy.

These results can all be derived as consequences of a single postulate regarding the behavior of the entropy as $T \to 0$.

7.2 THE THIRD LAW

The Third Law can be based on a number of different postulates. The one we choose is extracted from the third experimental observation stated above, that physical systems seek states of minimum entropy as the temperature is lowered. This observation leads to the postulate that is most immediately useful in materials science:

As the temperature approaches zero the molar entropy of any given system approaches the same finite least value for every equilibrium state.

The term given system in the statement of the Third Law is defined to include the constraints placed on the system, which may cause its entropy to approach a higher least value than would otherwise be reached. The constraints that are most important are the verbal constraints that formalize restrictions against transitions that are kinetically prevented from happening in practice. Examples of processes that are often forbidden include the low-temperature equilibration of crystal defects, such as vacancies, dislocations and grain boundaries, and low temperature structural transformations that require atom diffusion to occur.

7.3 THE LIMITING ENTROPY OF AN UNCONSTRAINED SYSTEM

Let a system be free of internal constraints, so that it can approach an unconstrained equilibrium. The entropy of every equilibrium state must be the same. Let the states of a single mole of the system be characterized by the coordinates $\{T, \{x\}\}$, where the $\{x\}$ are the mechanical and chemical geometric coordinates (chemical concentrations). The Third Law requires that

$$\lim_{T \to 0} \left[ \frac{\partial}{\partial x_k} S(T, \{x\}) \right] = 0$$

for all $x_k$ in $\{x\}$. Since this condition includes all ways of deforming the system or changing its composition, the molar entropy of an unconstrained system must approach a
constant value, $s_0$. Without loss of generality we can set $s_0 = 0$. Since the entropy is additive the entropy of $N$ moles of the system is just $Ns_0 = 0$. It follows that

*The entropy of an unconstrained system can be taken to vanish in the limit of zero temperature.*

This statement of the Third Law has two immediate and important consequences. First, consider the chemical reaction

$$A + B \rightleftharpoons C + D$$

which represents any reversible chemical reaction. The reaction can, by definition, come to equilibrium in an unconstrained system, so it must not change the entropy at zero temperature. It follows that *the entropy change in a chemical reaction vanishes at $T=0$*, in agreement with all experimental results known to date.

Second, consider the evolution of a multicomponent system as the temperature is lowered. If the equilibrium is unconstrained the entropy must vanish as $T \to 0$, which has the consequence that at sufficiently low temperature the system must evolve into a state with zero entropy or decompose into a mixture of phases that have zero entropy. As we shall see later (and most of us know already) a solid cannot have zero entropy unless its configurational entropy vanishes, that is, unless it is a pure component or perfectly ordered compound. It follows that *all solids order or decompose into mixtures of perfectly ordered phases in the limit of zero temperature.*

This result is particularly useful for constructing or evaluating equilibrium phase diagrams. Proposed diagrams that include solid solutions at low temperature cannot be correct. On the other hand, given only a knowledge of the ordered phases that appear in a system in the low-temperature limit one can often sketch a significant part of its equilibrium phase diagram.

### 7.4 The Unattainability of Zero Temperature

It follows from the Third Law that:

*It is impossible to cool a system to $T = 0$.*

To prove this statement let the system be characterized by the coordinates $\{S,\{q\}\}$. In the limit of zero temperature its entropy approaches the value $S_0$, which, to preserve generality, need not necessarily be zero. Since the constitutive coordinates can be varied independently all possible paths to zero temperature can be treated as the sum of two elementary processes: isometric changes in the entropy and isentropic changes in the geometric coordinates.
First let the temperature be decreased by an isometric change in the entropy. In a quasi-static transfer of heat,

$$\delta S = \frac{\delta Q}{T} = \left[ \frac{C_q}{T} \right] \delta T$$  \hspace{1cm} 7.4

from which,

$$\frac{\partial}{\partial T} [S^f(T, \{q\})] = \left[ \frac{C_q}{T} \right] > 0$$  \hspace{1cm} 7.5

It follows from equation 7.5 that the entropy of the system must decrease in any isometric process that decreases its temperature. But the only way to decrease the entropy isometrically is to transfer heat to a second system. The Second Law then requires that the total entropy change be positive. If \( r \) denotes the reservoir to which heat is transferred,

$$\delta S = \delta Q \left[ 1 - \frac{1}{T_r} \right] > 0$$  \hspace{1cm} 7.6

If the entropy is to decrease, \( \delta Q \) must be negative, so \( T_r \) must be less than \( T \). To lower the temperature to zero one requires a reservoir that already has \( T = 0 \). Since no such reservoir exists until the temperature of at least one system has been successfully decreased to zero, this method cannot be used.

Second, let the temperature be decreased by an isentropic change in the geometric coordinates. This process could only culminate in a state of zero temperature if it were possible to adjust the temperature of a system with finite temperature to the value, \( S_0 \), that is attained at zero temperature. But by the Third Law the entropy is independent of the values of the geometric coordinates at \( T = 0 \) and, by equation 7.5, the value of the entropy at finite temperature for any value of \( \{q\} \) is greater than that at \( T = 0 \). It follows that isentropic transitions cannot be used to reach zero temperature either, so \( T = 0 \) is unattainable.

Note that this result does not rule out an asymptotic approach to \( T = 0 \), as is gradually being achieved experimentally. For example, if the single geometric coordinate, \( q_k \), is varied isentropically then

$$dT = \left[ \frac{\partial T^f(S, \{q\})}{\partial q_k} \right] dq_k$$  \hspace{1cm} 7.7

The partial derivative \( (\partial T^f/\partial q_k) \) must vanish as \( T \to 0 \); otherwise an adiabatic change could be used to decrease the temperature from \( dT \) to zero. However, this coefficient may vanish as some power of the temperature. If, for example,

$$\left[ \frac{\partial T^f}{\partial q_k} \right] \propto T$$  \hspace{1cm} 7.8
in the limit $T \to 0$, then

$$T = Ae^{-q}$$  \hspace{1cm} 7.9$$

near $T = 0$, and $T$ vanishes asymptotically in the limit $q \to \infty$.

A behavior somewhat like this is exhibited by the magnetization of certain materials. The current record cold was achieved by adiabatic demagnetization.

### 7.5 THE ISOMETRIC SPECIFIC HEAT NEAR $T = 0$

Since it is possible to attain states with temperatures near zero, isometric transitions between these states can be used to measure the isometric specific heat in the limit, $T \to 0$. Let a system have molar entropy $s'$ and temperature $T'$. The change in entropy per mole on an isometric decrease in the temperature is

$$\Delta s = \int_{T}^{T'} \left[ \frac{c_q}{T} \right] dT$$  \hspace{1cm} 7.10$$

where $c_q$ is the isometric specific heat per mole. The integral approaches the limit

$$\lim_{T \to 0} (\Delta s) = s_0 - s'$$  \hspace{1cm} 7.11$$

But if $c_q$ does not vanish as $T \to 0$, that is, if $c_q$ approaches some constant, then the integral diverges and $s_0$ is undefined, which violates the Third Law. It follows that

$$\lim_{T \to 0} (c_q) = 0$$  \hspace{1cm} 7.12$$

The experimental data show that the condition 7.12 is obeyed for all known substances. Near $T = 0$, the isometric specific heat approaches the limit

$$c_q = AT^n$$  \hspace{1cm} 7.13$$

where $A$ is a constant and $n \geq 1$. This behavior is stronger than is needed to satisfy the Third Law, which only requires that $n > 0$.

The behavior of the other common thermodynamic properties near $T = 0$ is also restricted by the Third Law. We shall defer a specific discussion to the general discussion of equilibrium properties that appears below. However, the general rule is that those properties that are defined by differentiation with respect to the temperature vanish as $T \to 0$, while those whose definitions do not involve differentiation with respect to $T$ approach constant values that are independent of $T$. 

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*Notes on the Thermodynamics of Solids*, J.W. Morris, Jr.: Fall, 2008
### 7.6 The Behavior of Constrained Systems Near $T = 0$

When a system is prevented from reaching its most stable equilibrium by internal constraints then it may not be possible to set $s_0 = 0$. However, the Third Law has the consequence that the entropy remains defined and approaches a constant value as $T \to 0$. It can be shown that $s_0$ must be positive, since otherwise it would be possible to find an unconstrained equilibrium with $s_0 < 0$, in conflict with the Third Law. [I have not found a short, clean proof of this. The long, dirty proofs are too messy to include here.] Note that if $s_0$ is not zero the entropy depends on the size of the system at $T = 0$. The entropy of $N$ moles is, by the additive property,

$$S_0 = Ns_0 \quad 7.14$$

It follows that, if $S = S^\dagger(T, \{q\}, \{N\})$, where the $\{q\}$ are the mechanical geometric coordinates,

$$\lim_{T \to 0} \left[ \frac{\partial S^\dagger}{\partial q_k} \right] = 0 \quad 7.15$$

but the partial derivatives of $S^\dagger$ with respect to the $\{N\}$ do not vanish.

Most of the systems with which we deal in materials science are effectively constrained. In particular, those reconfigurations of the system that require diffusion or structural rearrangements are kinetically difficult at low temperature and usually do not occur. A cooled solid usually retains a finite grain boundary, dislocation and point defect density, and is often frozen into a metastable structural state. The defects in the crystal lattice always contribute a positive entropy at zero temperature. Solid solutions always have a positive configurational entropy. Structural metastability may or may increase the entropy. As we shall see, the entropy of any completely ordered state vanishes at $T = 0$, whether or not that state is metastable.

Thermodynamic behavior near $T = 0$ is the same whether or nor the system is constrained. Both the proof that $T = 0$ is unattainable and the proof that $c_q$ vanishes hold for constrained states.

### 7.7 Measurability of the Entropy

Using the Third Law the metric entropy of an unconstrained system can always be measured by determining its isometric specific heat as a function of temperature. Since $c_q$ vanishes at $T = 0$, the integral

$$S = \int_{0}^{T} \left[ \frac{C_q}{T} \right] \, dT' \quad 7.16$$
determines the entropy of an isometric reference state at temperature $T$. The entropy of other states can then be measured by relating them to the isometric states by quasi-static adiabatic transitions.

In the case of a constrained system, equation 7.16 yields the entropy difference, $S - S_0$. The value of $S_0$ can be found experimentally by applying equation 7.16 to both the constrained and unconstrained examples of the system, and measuring the entropy change when the constraints are relaxed at a temperature that is high enough that equilibrium is reached spontaneously.