

The Nernst Postulate: The Third Law of Thermodynamics

For every complex problem there is an answer that is clear, simple, and wrong.

H. L. Mencken, American journalist (1880–1956)

In the early part of the twentieth century the German chemist and physicist Walther Hermann Nernst (1884–1941) formulated the ‘Nernst Postulate’. It has also become known as the Third Law of Thermodynamics, due to its importance.

The Nernst Postulate: The entropy of a thermodynamic system goes to a constant as the temperature goes to zero.

This postulate has far-reaching consequences. Most directly, it puts important constraints on the behavior of real systems at low temperatures. Even more importantly, in its universal applicability, it reveals the pervasive influence of quantum mechanics on macroscopic phenomena.

18.1 Classical Ideal Gas Violates the Nernst Postulate

Since we have only discussed classical statistical mechanics so far in this book, the Nernst Postulate might seem rather startling. The results for the classical ideal gas that we derived in Part I are completely inconsistent with it. To see this, consider eq. (7.2) for the entropy of the classical ideal gas,

$$S(U, V, N) = kN \left[\frac{3}{2} \ln \left(\frac{U}{N} \right) + \ln \left(\frac{V}{N} \right) + X \right]. \quad (18.1)$$

If we insert the equation of state for the energy,

$$U = \frac{3}{2} N k_B T, \quad (18.2)$$

we find an equation for the entropy as a function of temperature,

$$S(T, V, N) = kN \left[\frac{3}{2} \ln \left(\frac{3k_B T}{2} \right) + \ln \left(\frac{V}{N} \right) + X \right]. \quad (18.3)$$

Since $\ln T \rightarrow -\infty$ as $T \rightarrow 0$, the entropy of the classical ideal gas does not go to a constant at zero temperature. In fact, it will be shown in Chapter 19 that the entropies of all classical systems go to $-\infty$ at zero temperature.

The reason for the validity of the Nernst Postulate for real systems lies entirely in quantum statistical mechanics, and will be derived in Chapter 23.

18.2 Planck's Form of the Nernst Postulate

Extending the Nernst Postulate, Max Planck made the stronger statement that the entropy should not only go to a constant, but that the constant must be zero. This is, indeed, the form in which the Nernst Postulate is usually remembered—which is unfortunate, since it is not entirely true. Although Nernst's formulation of his postulate is true for all quantum mechanical models and all real systems, Planck's version is not always valid.

We will return to a justification of the Nernst Postulate and a discussion of Planck's alternative in Chapter 23 on quantum statistical mechanics.

18.3 Consequences of the Nernst Postulate

Why is the Nernst Postulate important? One of the main reasons is that it places severe limits on the low-temperature behavior of the specific heat and the coefficient of thermal expansion.

18.3.1 Specific Heat at Low Temperatures

The first consequence of the Nernst Postulate is that the specific heat of anything must go to zero at zero temperature.

To prove this statement, use the connection between a small amount of heat, dQ , added to a system and the corresponding change in entropy, dS , in eq. (10.23),

$$dS = \frac{dQ}{T}. \quad (18.4)$$

We can relate the change of temperature to dQ through the specific heat, which is defined in Section 14.4 as

$$c_X(T) = \frac{T}{N} \left(\frac{\partial S}{\partial T} \right)_{X,N}, \quad (18.5)$$

where X stands for either V or P , depending on which is held constant for the experiment in question. The heat added is therefore

$$dQ = Nc_X(T)dT, \quad (18.6)$$

where we have explicitly indicated the temperature-dependence of the specific heat. Putting eqs. (18.4) and (18.6) together and integrating, we find an expression for the change in entropy between the temperatures T_1 and T_2 ,

$$S(T_2) - S(T_1) = \int_1^2 \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{c_X(T)}{T} dT. \quad (18.7)$$

Now suppose that the specific heat went to a constant in the limit of zero temperature,

$$\lim_{T \rightarrow 0} c_X(T) = c_o. \quad (18.8)$$

Then, for sufficiently low temperatures, we could approximate the specific heat by c_o to calculate the change in entropy,

$$S(T_2) - S(T_1) \approx \int_{T_1}^{T_2} \frac{c_o}{T} dT = c_o(\ln T_2 - \ln T_1). \quad (18.9)$$

In the limit that T_1 goes to zero, eq. (18.9) implies that $S(T_2) - S(T_1) = \infty$, which contradicts the Nernst Postulate. Therefore, the Nernst Postulate requires that the specific heat of anything go to zero at zero temperature.

We have already seen $\lim_{T \rightarrow 0} S(T) = -\infty$ for the classical ideal gas, so that it violates the Nernst Postulate. This can also be seen from the fact that the specific heat at constant volume does not go to zero at zero temperature, but instead has the constant value $c_V = (3/2)k_B$.

18.4 Coefficient of Thermal Expansion at Low Temperatures

Another consequence of the Nernst Postulate is that the coefficient of thermal expansion, defined in Section 14.4 as

$$\alpha(T) = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P,N}, \quad (18.10)$$

must also vanish at zero temperature. To see why this is true, note that a Maxwell relation that can be derived from

$$dG = -SdT + VdP + \mu dN, \quad (18.11)$$

gives us a relationship between a derivative of the entropy and the coefficient of thermal expansion,

$$\left(\frac{\partial S}{\partial P}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{P,N} = -V\alpha(T). \quad (18.12)$$

If the entropy goes to a constant that is independent of pressure, this gives us

$$\lim_{T \rightarrow 0} \alpha(T) = 0. \quad (18.13)$$

18.5 The Impossibility of Attaining a Temperature of Absolute Zero

It is often stated that a temperature of absolute zero is unattainable *because* of the Third Law of Thermodynamics. This is incorrect.

Classical statistical mechanics prohibits the attainment of $T = 0$ because it would require an infinite amount of energy. Quantum statistical mechanics actually makes it easier to achieve a low temperature, so that it would only require a finite amount of energy to achieve $T = 0$.

In both quantum and classical statistical mechanics, any process that would achieve $T = 0$ would require an infinite number of steps, so that it could not be completed in a finite amount of time.

The Nernst Postulate makes it easier to achieve low temperatures by making specific heats go to zero, as discussed in Section 18.3.1. Because of the equation

$$C = \frac{dQ}{dT}, \quad (18.14)$$

if we wish to lower the temperature by dT , it requires removing from the system of interest an amount of energy

$$dQ = C dT. \quad (18.15)$$

The larger the specific heat, C , the more energy must be removed from the system to lower the temperature by a given value of dT . Since the Nernst postulate requires $C \rightarrow 0$, as $T \rightarrow 0$, lowering the temperature is easier with the Nernst Postulate (quantum statistical mechanics) than it is without the Nernst Postulate (classical statistical mechanics).

These ideas will be explored further in the problems at the end of this chapter.

18.6 Summary and Signposts

In Part I of this book we developed the foundations of classical statistical mechanics based on the existence of atoms and some assumptions about model probabilities. We

followed Boltzmann in defining the entropy in terms of the logarithm of the probability distribution of macroscopic observables in a composite system, and we derived a general formula for the entropy of a classical system of interacting particles. For the special case of non-interacting particles (the classical ideal gas), we explicitly evaluated the entropy as a function of energy, volume, and number of particles.

In Part II we developed the theory of thermodynamics on the basis of the general properties of the entropy that we found in Part I. This led us to develop powerful methods for generating exact relationships between measurable thermodynamic quantities.

With this chapter we come to the end of our introduction to thermodynamics, and with it the end of Part II of the book.

We have seen the power of thermodynamics in relating physical properties that, at first glance, might seem entirely unrelated to each other. On the other hand, we have seen that thermodynamics makes almost no predictions about the actual value of any quantity. Indeed, the main exceptions are the predictions for the vanishing of the specific heat and the coefficient of thermal expansion at zero temperature.

Up to this point, the emphasis has been on the concepts in thermal physics and their consequences for relationships between measurable quantities. In the remainder of the book we will develop more powerful methods for carrying out practical calculations in statistical mechanics.

Part III will discuss classical statistical mechanics, introducing the canonical ensemble, which is the workhorse of the field. It will also return to the question of irreversibility and the uniqueness of the model probability assumptions we made in setting up the foundations of statistical mechanics.

Part IV will discuss quantum statistical mechanics, including black-body radiation, and Bose–Einstein and Fermi–Dirac statistics. It will also show how quantum mechanics leads naturally to the Nernst Postulate. The book will end with an introduction to the theory of phase transitions, using the Ising model as an illustration.

By the end of the book you should have a good foundation in both thermodynamics and statistical mechanics—but it will still be only a foundation. The entire field of condensed-matter physics will be open to you, with all its complexity and surprises. May you enjoy your further explorations in this fascinating area.

18.7 Problems

PROBLEM 18.1

Is a temperature of absolute zero attainable?

The Third Law of Thermodynamics (the Nernst postulate) requires the heat capacity of any object to go to zero as the temperature goes to absolute zero. It is often stated in thermodynamics textbooks that the third law of thermodynamics also prohibits the attainment of a temperature of absolute zero. In this problem we will consider to what extent that claim is correct. If it is correct, that would mean that a temperature of absolute zero could be obtained if the Nernst postulate were not valid.

We will examine the consequences of a heat capacity that does not go to zero as the temperature goes to zero.

To simplify the argument, we will assume that we have two objects, A and B , with constant, non-zero heat capacities C_A and C_B . We will also assume that we have an ideal heat engine at our disposal.

1. Assume that the initial temperatures of the two objects are $T_{A,i} > 0$ and $T_{B,i} > 0$. Calculate the total work required to reduce the temperature of object A to absolute zero.
2. Now let the object B become infinite, so that it acts as a heat reservoir, and its temperature does not increase during the process. Again calculate the total work required to reduce the temperature of object A to absolute zero.
3. For the third part of this problem, consider again two *finite* objects, A and B . Assume that $C_A(T) \propto T^\alpha$, and $C_B(T) \propto T^\alpha$, where $\alpha > 0$ is a positive constant. Since $C_A(T) \rightarrow 0$ as $T \rightarrow 0$, this is consistent with the third law. We will see later in the course that materials with $\alpha = 1$ and $\alpha = 3$ really do exist. Again calculate the total work required to reduce the temperature of object A to absolute zero.

.....