CHAPTER 3
THE THIRD LAW OF THERMODYNAMICS[1]

In sharp contrast to the first two laws, the third law of thermodynamics can be characterized by diverse expression[2], disputed descent, and questioned authority.[3] Since first advanced by Nernst[4] in 1906 as the Heat Theorem, its thermodynamic status has been controversial; its usefulness, however, is unquestioned.

3.1 THE HEAT THEOREM

The Heat Theorem was first proposed as an empirical generalization based on the temperature dependence of the internal energy change, ΔU, and the Helmholtz free energy change, ΔA, for chemical reactions involving condensed phases. As the absolute temperature, T, approaches zero, ΔU and ΔA by definition become equal, but The Heat Theorem stated that $\mathrm{d}\Delta U/\mathrm{d}T$ and $\mathrm{d}\Delta A/\mathrm{d}T$ also approach zero. These derivatives are ΔC_v and $-\Delta S$ respectively. The statement that ΔC_v equals zero would attract little attention today in view of the abundance of experimental and theoretical evidence showing that the heat capacities of condensed phases approach zero as zero absolute temperature is approached. However, even today the controversial and enigmatic aspect of The Heat Theorem is the equivalent statement

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[1] Most of this chapter is taken from B.G. Kyle, *Chem. Eng. Ed.*, *28(3)*, 176 (1994).

[2] For a sampling of expressions see E. M. Loebl, *J. Chem. Educ.*, *37*, 361 (1960).

[3] For extreme positions see E. D. Eastman, *Chem. Rev.*, *18*, 257 (1936).

[4] All of Nernst's work in this area is covered in W. Nernst, *The New Heat Theorem*; Dutton: New York, 1926.

$$\lim_{T \to 0} \Delta S = 0 \qquad\qquad \textbf{(3-1)}$$

In 1912 Nernst offered a proof that the unattainability of zero absolute temperature was dictated by the second law of thermodynamics and was able to show that Eq. (3-1) follows from the unattainability principle. The latter result seems undisputed, but Nernst was unable to convince his contemporaries of the thermodynamic grounding of the unattainability principle.

Many years of low-temperature research have firmly established the credibility of the unattainability principle and as a result it has been proposed as the third law of thermodynamics. This proposal has the merit of having all three laws expressed in phenomenological language and, of course, it leads to the useful result stated in Eq. (3-1).

As a matter of convenience, it is possible to express ΔS for a process under consideration in terms of entropies of formation of participating species because in such a calculation there is a cancellation of the entropies of the constituent elements. For this reason the entropy of an element may be assigned any value. According to Eq. (3-1), at zero absolute temperature the entropy changes for formation reactions will be zero and it is convenient to set elemental entropies equal to zero as recommended by Lewis and Randall.[5] This results in the familiar statement that the entropy of every perfect crystalline substance can be taken as zero at zero absolute temperature and is, of course, the convention employed in the determination of "absolute" entropies.

3.2 CONFORMANCES, EXCEPTIONS, AND INTERPRETATIONS

Undoubtedly the most convincing confirmation of the Heat Theorem involved the calculation of absolute entropies from calorimetric measurements on pure substances which were then used to calculate entropy changes for chemical reactions. These calculated values were in agreement with entropy changes determined from the temperature dependence of experimentally measured equilibrium constants.[6] Later, it was shown through the use of

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[5] G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill, New York, 1923, Chap. 31.

[6] Other successful applications of the third law are given by K. Denbigh, *The Principles of Chemical Equilibrium*, 3rd ed., Cambridge University Press, Cambridge, 1971, Chap. 13.

quantum statistical mechanics that spectroscopic data could be used to calculate absolute entropies in excellent agreement with those calculated from calorimetric data.[7] Quantum statistical mechanics also provides the microscopic interpretation of zero entropy for a perfect crystal as well as quantitative corrections for those few errant substances exhibiting small positive entropy values at zero absolute temperature. The statement that the lowest energy state of the crystal is nondegenerate (only a single quantum state is available to it) is easily visualized as a perfectly ordered crystal where only a single arrangement of atoms, molecules, or ions on the crystal lattice is possible. Thus, in terms of Boltzmann's famous equation

$$S = k \ln \Omega \tag{3-2}$$

it may be stated that for $\Omega_o = 1$ at $T = 0$ the entropy, S_o, is zero.

Exceptions to S_o equal to zero are explained in terms of "frozen-in" disorder. For example, a linear molecule such as carbon monoxide can take two possible orientations on a lattice site, CO or OC. Orientations on adjacent sites such as COOC or OCCO represent a slightly higher energy state than ordered orientations such as COCO and are therefore favored at higher temperatures. While there is a tendency for the crystal to move toward the low-energy, ordered state on cooling, the rate at which molecular orientations proceed slows to a standstill and a state of "frozen-in" disorder results at zero absolute temperature. If the orientations of the CO molecule were completely random, there would be 2^N possible configurations on a lattice of N sites (two possibilities per site). Setting $\Omega_o = 2^N$ in Eq. (3-2) leads to $S_o = R\ln 2$ which is also seen to be the entropy change on forming an equimolar binary mixture.[8] The value of $R\ln 2$ is extremely close to the observed difference between calorimetric and spectroscopic absolute entropies.

The vast majority of substances conform to S_o equal to zero and can be visualized as forming crystals of perfect order ($\Omega_o = 1$). The few exceptions can be explained in terms of "frozen-in" disorder in a manner similar to that described for carbon monoxide. Here there is seen to be a close correspondence between

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[7] See Sec. 3-6.

[8] See Eq. (14-22) of this textbook.

entropy and disorder in a spatial sense. Unfortunately, there are other systems conforming to the Heat Theorem that place a strain on this interpretation. We now examine these systems.

Measurements of phase equilibrium data for pure substances show that the slope of the solid-vapor coexistence curve for many substances and the slope of the liquid-vapor coexistence curves for ^{4}He and ^{3}He approach zero as zero absolute temperature is approached.[9] From the Clapeyron equation,

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta v}$$

$$(3\text{-}3)$$

and the fact that Δv is finite, we obtain the result that $\Delta S = 0$ and conclude that Eq. (3-1) applies to these phase changes. Both helium isotopes remain liquid under their own vapor pressure down to zero Kelvin and both require a pressure considerably higher than their vapor pressures in order to form a solid phase and the appropriate calculations show[10] that Eq. (3-1) also applies to the solid-liquid phase transition. Thus, if the Lewis and Randall convention is used, the entropies of pure liquids and vapors also have zero entropies. While it may be possible to argue that these systems are nondegenerate in their lowest energy state, the simple picture of zero entropy corresponding to perfect order does not seem appropriate, at least in a physical sense.

The interpretation is further strained when the behavior of glasses in the low-temperature limit is considered. The Maxwell relationship

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$(3\text{-}4)$$

together with Eq. (3-1) leads to

$$\lim_{T \to 0}\left(\frac{\partial V}{\partial T}\right)_P = 0$$

$$(3\text{-}5)$$

Thermal coefficients of expansion for many substances have been measured at

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[9] J. A. Beattie and I. Oppenheim, *Principles of Thermodynamics*; Elsevier, Amsterdam, 1979, Chap. 11.

[10] *ibid.*

temperatures approaching absolute zero. As expected, Eq. (3-5) is obeyed by crystalline solids, but one may be surprised to learn that it is also obeyed by glasses.[11] Here a microscopic physical interpretation hardly seems possible.

Systems comprised of liquids, vapors, and glasses strain to the breaking point the putative association of zero entropy with perfect spatial order. These are the systems that prompt us to ask *Is there a microscopic physical interpretation of the Heat Theorem applicable to all systems?* One could argue that the association of entropy with spatial order is naive and that $\Omega_0 = 1$ only means that the system is nondegenerate. For example, both Fermi-Dirac and Bose-Einstein gases have been shown to be nondegenerate[12] and therefore have $S_o = 0$. In the case of crystalline solids $\Omega_o = 1$ can be interpreted physically as spatial order, but no such microscopic description of the gases in physical terms is possible. Instead Ω_o can only be seen as a logical construct that allows a mathematical treatment of the system. The answer to the question is *No! only an explanation in logical terms is possible.* This is yet another instance of our inability to obtain a microscopic view of entropy in anything other than logical terms.

If there is no physical microscopic interpretation of the Heat Theorem, then what is the basis for its existence? As will be shown below, the answer is that Eq. (3-1) is dictated by the logical structure of thermodynamics.

3.3 THE CLASSICAL THERMODYNAMIC VIEW

The absolute temperature scale is defined in terms of the performance of a Carnot engine

$$\frac{T_1}{T_2} = \frac{|Q_1|}{|Q_2|} \qquad\qquad \textbf{(3-6)}$$

where $|Q_2|$ is the input heat at T_2 and $|Q_1|$ is rejected heat at T_1. Instrumental in the derivation of Eq. (3-6) is a second-law statement such as *It is impossible to*

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[11] G. K. White, *Cryogenics*, *4*, 2 (1964).

[12] A. H. Wilson, *Thermodynamics and Statistical Mechanics*, Cambridge University Press, Cambridge, 1957, Chap. 6.

completely convert heat into work in a cyclic process. Equation (3-6) is therefore subject to this constraint and would not be valid for $T_1 = 0$ where $|Q_1|$ would be zero. Therefore, the logical structure of thermodynamics does not permit zero absolute temperature and since the laws of thermodynamics are based on statements from the physical world and have proven reliable in dealing with the physical world, it may be stated that zero absolute temperature is unattainable. Thus, it is not necessary to propose the unattainability principle as a third law of thermodynamics.

Equation (3-1) can be derived from the unattainability principle[13] by considering the arbitrary process $\alpha \rightarrow \beta$ which could be a chemical or physical transformation or a change in a thermodynamic property (e.g., intensity of magnetization). The entropies of the system in these states are

$$S^\alpha = S_0^\alpha + \int_0^T \frac{C_\alpha}{T}\, dT \tag{3-7a}$$

$$S^\beta = S_0^\beta + \int_0^T \frac{C_\beta}{T}\, dT \tag{3-7b}$$

The mathematical formalism of thermodynamics allows these equations to be written as if $T = 0$ were possible. However, a more rigorous approach that uses the limit as T approaches zero yields the same result.[14]

For a reversible adiabatic process between states α and β occurring near zero absolute temperature, we utilize Eq. (3-7) to write

$$S_0^\alpha + \int_0^{T'} \frac{C_\alpha}{T}\, dT = S_0^\beta + \int_0^{T''} \frac{C_\beta}{T}\, dT \tag{3-8}$$

If the process began in state α at T' and ended in state β at $T'' = 0$ we would have

$$S_0^\beta - S_0^\alpha = \int_0^{T'} \frac{C_\alpha}{T}\, dT > 0 \tag{3-9}$$

but because $T'' = 0$ is not possible, the following holds

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    [13] R. Fowler and E. A. Guggenheim, *Statistical Thermodynamics*, Cambridge University Press, London, 1956, Chap. 5.

    [14] See Appendix 3A.

$$S_0^\beta - S_0^\alpha \leq 0 \tag{3-10}$$

Considering the reverse process that proceeds from T'' to $T' = 0$, we can, in the same manner, show that it is necessary for

$$S_0^\beta - S_0^\alpha \geq 0 \tag{3-11}$$

These two inequalities can be satisfied only when $S_0^\beta = S_0^\alpha$ and it is seen that Eq. (3-1) follows from the unattainability principle. Thus, Eq. (3-1) arises from the second law and is needed to preserve the logical structure of thermodynamics; a third law is therefore unnecessary.

3.4 ADDRESSING PREVIOUS ARGUMENTS

Two types of arguments found in the literature should be addressed: those that attempt to show that the attainment of zero absolute temperature is not prohibited by the second law and those that attempt to show that existence of a reservoir at zero absolute temperature does not threaten the second law.

By applying the mathematical formalism of thermodynamics down to and including zero absolute temperature, it has been shown that this temperature can be reached in a finite number of steps[15] or that the work required to reduce a system[16] to this temperature is finite.[17] As shown in Appendix 3A, the mathematical formalism is such that the use of $T = 0$ as a lower limit of integration gives the appearance of being permissible. A similar condition probably obtains for these arguments which, despite their apparent cogency, are incomplete because the possibility that the existence of a reservoir at zero absolute temperature might pose a threat to the second law was not examined.

Nernst's proof that the unattainability principle is required by the second law was based on the argument that if a reservoir at zero absolute temperature existed, it would be possible to operate a Carnot engine using this reservoir to

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[15] F. E. Simon, *Low Temperature Physics*, Academic Press, London, 1952, Chap. 1.

[16] The heat capacity of the system was assumed to follow Eq.(3-12) of Appendix 3A.

[17] E.M.Loebl, *op. cit.*

convert heat taken in at a higher temperature completely into work. This is essentially the argument presented here. The two most damaging objections against this position were based on possible operating difficulties associated with the Carnot cycle.[18] [19] [20]

The first objection calls into question the possibility of carrying out an isothermal process at zero absolute temperature because the effects of heat leaks and frictional heat are much more pronounced at this extreme. This is an objection of degree rather than principle and should carry no weight when it is recognized that the logical structure constituting thermodynamics rests on such idealizations as reversibility, isothermality, and adiabaticity. As these idealizations can never be realized in the physical world, it seems pointless to argue that they would be more difficult to achieve at low temperature.

The second objection points to the ambiguity associated with the isothermal step in the Carnot cycle presumed to occur at zero absolute temperature. Because no heat is rejected, this step would be adiabatic as well as isothermal but it would not necessarily be isentropic for it can only be said that the entropy change is $0/0$. It has been argued that when a system attempting to follow a Carnot cycle reaches zero absolute temperature the second law is not threatened because there is no assurance that the system would take the isothermal path and complete the cycle rather than take the adiabatic path and return to a previous state. The emphasis here is misplaced! Because a single violation would vitiate the second law, concern should be directed to the possibility, no matter how small, that the system would take the isothermal path. There is no assurance that this would not occur and therefore the unattainability principle is needed.

Both of these inoperability objections seem to demand a premature reality check. It could be argued that the Carnot engine is simply a concept that is part of the logical, mathematical formalism of thermodynamics and it is rather the

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[18] P. S. Epstein, *Textbook of Thermodynamics*, Wiley, New York, 1937, Chap. 15.

[19] A. B. Pippard, *The Elements of Classical Thermodynamics*, Cambridge University Press, London, 1957, Chap. 5.

[20] M. L. Boas, *Am. J. Phys.*, *28*, 675 (1960).

final result of the argument which should be subjected to a reality check. In this regard it should be noted that the observed conformance to Eq. (3-5) may be taken as proof that the concept of a Carnot engine is viable in the limit as T approaches zero. This is because the Maxwell relation, Eq. (3-4), can be derived through the agency of a Carnot cycle as was originally shown by Maxwell himself.[21]

3.5 THE STATUS AND INTERPRETATION OF THE THIRD LAW

We have seen that Eq. (3-1) can be understood only in a logical sense and to that end a derivation showing its descent from the second law has been presented. As this derivation is essentially an elaboration of Nernst's original derivation which was never fully accepted, it is reasonable to expect that it could suffer the same fate. However, whether Eq. (3-1) is regarded as deriving from the second law or whether it is regarded as an additional statement required to save the second law, it is still possible to see it as a logical requirement. It could be stated that Eq. (3-1) is necessary to define the limiting entropy change which we have seen would have the indeterminate form $0/0$ otherwise. By reversing the argument presented in Sec. 3.3, it is easily seen that the unattainability principle follows from Eq. (3-1).

Although Eq. (3-1) has now been given thermodynamic justification, its exceptions seem uncomfortably numerous for a thermodynamic relationship and it is therefore appropriate to examine its applicability. This problem has been addressed by Simon[22] and resolved by the following statement:

> "At absolute zero the entropy differences vanish between all those states of a system between which a reversible transition is possible *in principle* even at the lowest temperatures."

Simon's statement is completely general, however, in regard to the behavior of glasses the statement of Fowler and Guggenheim[23] is more specific.

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[21] L. K. Nash, *J. Chem. Educ.*, *41*, 368 (1964).

[22] F. E. Simon, *Physica*, *10*, 1089 (1937).

[23] *op. cit.*

"For any isothermal process involving only phases in internal equilibrium or, alternatively, if any phase is in frozen metastable equilibrium, provided the process does not disturb this frozen equilibrium, $\lim_{T \to 0} \Delta S = 0$."

Simon assigned unquestioned thermodynamic status to Eq. (3-1) and pointed out that the restrictions made explicit in his statement are implicitly made in applying any other thermodynamic relationship. The question is not whether Eq. (3-1) is valid, but rather whether the application of thermodynamics to a particular system is valid. Valid thermodynamic systems must exist in equilibrium states and thus be capable of undergoing reversible processes. As Eq. (3-1) is applied only under the most stringent conditions where "frozen-in," nonequilibrium states are not unexpected, it is natural that it will not seem to possess the unexceptional status accorded to the other laws and relations of thermodynamics. However, this is a problem in the application of thermodynamics and should not call the validity of Eq. (3-1) into question.

Because of the widespread use of the Lewis and Randall convention leading to the convenience of "absolute" entropies and because of the remarkable success in calculating these values via the methods of quantum statistical mechanics, we are tempted to regard entropy as an intrinsic property of matter and thereby seek a physical microscopic interpretation. However, we have seen for the case of liquids, gases, and glasses that this is not a fruitful approach.

Equation (3-1) is the most general statement and has been shown to be simply a necessary logical statement. This suggests the view that entropy is merely a defined state function embedded in the logical-mathematical structure of thermodynamics. Thus, it seems appropriate that quantum statistical mechanics yields a representation of entropy in logical rather than physical terms. Because classical thermodynamics neither provides nor requires physical visualization of its functions, entropy is no less useful for want of a microscopic physical interpretation. While this view does not provide the physical insight available through a microscopic interpretation, it is at least free of contradictions.

3.6 ABSOLUTE ENTROPIES

If the requisite calorimetric data are available, the entropy of an ideal gas can, in general, be calculated from

$$S = S_o + \int_0^{T_F} \frac{C_P(c)}{T} \, dT + \frac{\Delta h^F}{T_F} + \int_{T_F}^{T_V} \frac{C_P(l)}{T} \, dT + \frac{\Delta h^V}{T_V} + \int_{T_V}^{T} \frac{C_P(g)}{T} \, dT$$

where $C_P(c)$, $C_P(l)$, and $C_P(g)$ are the heat capacities of the crystalline, liquid, and gas phases, Δh^F and Δh^V are the latent heats of fusion and vaporization, and T_F and T_V are the corresponding phase transition temperatures. We have already seen that when elements are assigned zero entropy at zero absolute temperature, the third law specifies the entropy of any substance, S_o, to be zero at this condition. This convention allows values of "absolute" entropy to be calculated from calorimetric data via the above equation. This is a convenience and not a necessity. In fact, in using this convention the isotope effect has been ignored.

Most elements consist of a mixture of isotopes. From the microscopic point of view, there will be many possible arrangements of these sets of distinguishable particles on the crystal lattice and therefore Ω_o will be significantly greater than unity. From a macroscopic point of view, we would simply say that there is an entropy of mixing to be considered. Because the isotopic composition of the elements is now well known, the isotopic effect could be dealt with quantitatively. However, as a practical matter it is not necessary to do so because the isotopic composition is expected to remain constant for processes of thermodynamic interest and therefore any correction for this effect would cancel on determining an entropy change.

Using quantum statistical mechanics the Sackur-Tetrode equation, Eq. (2-21), for the entropy of a monatomic ideal gas was derived in Sec. 2.3.2.

$$S = Nk \left[\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) + \frac{5}{2} \right] \qquad \textbf{(2-21)}$$

This equation yields absolute entropy values in excellent agreement with calorimetric values. Since most of the noble gases are isotopic mixtures, this situation must be considered in applying Eq. (2-21). As Eq. (2-21) shows a dependence of entropy on particle mass, the entropy of each isotope can be calculated separately and a weighted average determined for the mixture. Consistent with the convention used for the calorimetric absolute entropy, the entropy of mixing the isotopes is ignored. Thus, "absolute" entropies are not absolute.

While the concept of absolute entropy derives from the third law and the Sackur-Tetrode equation yields excellent values of absolute entropy, it will be

noticed that it does not show the expected behavior as absolute zero temperature is approached. Instead of approaching zero, the Sackur-Tetrode entropy becomes negatively infinite in this limit. This discrepancy is resolved by the quantum statistical mechanical treatment of ideal gases at extremely low temperatures[24] where it is necessary to use different types of statistics. The rules for determining probabilities of quantum states as given in Sec. 2.1 characterize Maxwell-Boltzmann statistics. While this statistical scheme works well for most problems of thermodynamic interest, it fails at very low temperatures where it becomes necessary to use different schemes for determining the probability of quantum states. There are two of these schemes: Fermi-Dirac statistics and Bose-Einstein statistics. Both of these statistics when applied to ideal gases yield expressions showing vanishing entropy at zero absolute temperature. These entropy expressions are relatively complex, but reduce to the Sackur-Tetrode equation at higher temperatures. In this sense, the Sackur-Tetrode equation can be considered consistent with the third law.

As the Sackur-Tetrode equation applies to monatomic gases whose energy can be manifested only as translational energy, a different approach is needed for polyatomic gases. In accounting for the energy of molecules, it is necessary to include contributions due to the rotation of the molecule and to vibrations between atoms within the molecule as well as translational energy. Each mode of energy is quantized and the energy levels for the rotational and vibrational modes can be calculated from spectroscopic data. Because it is assumed that translational, rotational, and vibrational energy modes are independent, the total energy is additive and the partition function can be written as a product of the translational, rotational, and vibrational partition functions. The thermodynamic functions are expressed in terms of the logarithm of the partition function and therefore the contributions to them from the various energy modes are additive.[25] Absolute entropies calculated in this manner are in excellent agreement with calorimetric values and are actually considered to be more reliable. Most ideal-gas thermodynamic property tabulations are based on calculation from spectroscopic data.

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[24] A.H.Wilson, *op. cit.*

[25] Details for calculation of thermodynamic properties from spectroscopic data are available in G.N. Lewis, M. Randall, K.S. Pitzer, and L.Brewer, *Thermodynamics*, McGraw-Hill, New York, 1961, Chap. 27.

APPENDIX 3A
ENTROPY CHANGES NEAR ABSOLUTE ZERO

For a heat capacity of the form

$$C = \alpha T^{\beta} \quad \begin{matrix} (\alpha > 0) \\ (\beta > 0) \end{matrix} \qquad \textbf{(3-12)}$$

the entropy change between an extremely low temperature, ε, and the temperature of interest, T, is

$$S - S_{\varepsilon} = \int_{\varepsilon}^{T} \frac{\alpha T^{\beta}}{T} \, dT = \frac{\alpha}{\beta} (T^{\beta} - \varepsilon^{\beta}) \qquad \textbf{(3-13)}$$

and the limit as ε approaches zero is

$$\lim_{\varepsilon \to 0} (S - S_{\varepsilon}) = \frac{\alpha}{\beta} T^{\beta} = \int_{0}^{T} \frac{C}{T} \, dT \qquad \textbf{(3-14)}$$

which is seen to be the result obtained by using $T = 0$ as the lower limit of integration.