Some Comments on the Third and Second Laws of Thermodynamics

The Nernst Heat Theorem is a common and useful expression of the Third Law of Thermodynamics. It states that the difference in entropy between two equilibrium states at temperature $T$ approaches zero as the absolute temperature approaches zero, i.e.,

$$\lim_{T \to 0} \Delta S = \lim_{T \to 0} [S(T,x) - S(T,x')] = 0 \quad (1)$$

where $x$ stands for the set of intensive properties which must be specified together with $T$ to determine the state of the system.

In many texts the Third Law is also written as the statement that zero temperature is unattainable. But the proofs of the equivalency between the two statements of the Third Law have been limited to adiabatic processes. In this paper, a general proof of this equivalency is given.

Proof of Equivalence

For simplicity we shall consider one component, homogeneous systems whose thermodynamic states are determined by specifying the number of moles present, the temperature $T$, and either the pressure $P$ or the volume $V$. It is easy to extend our results to more complicated systems. We shall assume that the entropy $S$ of the system does depend on the temperature. Under these circumstances, it follows from the stability considerations that

$$S(T,P) - S(T',P) > 0$$
$$S(T,V) - S(T',V) > 0 \quad (2)$$

For $T > T'$. Equation (2) is essential for the proof that follows.

We are now ready to prove that the Nernst theorem is equivalent to the assertion of unattainability. We consider a process which produces a change in state from the state $A$, specified by $T_A > 0$ and $P_A$ (or $V_A$), to the state $B$, specified by $T_B = 0$ and $P_B$ (or $V_B$). The entropy change for this change in state is

$$\Delta S = S_B - S_A \quad (3)$$

and can be written as

$$\Delta S = S_B^o - S_A^o - (S_A - S_A^o) \quad (4)$$

where

$$S_B^o = \lim_{T \to 0} S(T,P_B)$$

and $S_A^o$ is similarly defined. If the Nernst theorem is applied,

$$S_B^o - S_A^o = 0. \quad (5)$$

Thus, eqns. (2) and (4) yield the result

$$\Delta S = -(S_A - S_A^o) = -\Gamma_A < 0 \quad (6)$$

where

$$\Gamma_A \equiv S_A - S_A^o > 0 \quad (7)$$

Note that we have proved that the entropy change in going from any state at finite $T$ to any state at $T = 0$ is negative.

The Second Law states that

$$\Delta S \geq \int_A^B \frac{dQ}{T} \quad (8)$$

A stronger statement is attributed to Planck. It asserts that for equilibrium states at $T = 0, S = 0$.


1 This mathematical statement of the Second Law is derived from physical statements under the assertion that isotherms cannot be adiabats (see Kirkwood, J. G., and Oppenheim, I., "Chemical Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1961). The next section contains a proof of this assumption.
equation (6), proves that no adiabatic path, either reversible or irreversible, can lead from a state at finite T to a state at T = 0.

Since T_A can be chosen to be as close to zero as we wish, eqns. (6) and (8) imply that dQ must be less than zero in the last portion of the process leading to T = 0°C. But from the definition of heat as energy which flows from a system of higher temperature to a system at lower temperature as a consequence of the temperature difference, if dQ < 0 there must exist some external temperature, T_e, such that T_e is less than the temperature of the system. Therefore, the Nernst Theorem does imply that T = 0 is unattainable.

Next we prove that the assertion of unattainability implies the Nernst Theorem. It was noted that if process AB occurs, ΔS cannot be negative. Hence, from eqn. (4) and the unattainability premise

\[ \Delta S < 0 \]

and

\[ S_{B}^o - S_{A}^o < \Gamma_A > 0. \]  

Similarly, if we consider a process B'A' where the state B' is specified by T_{B'} > 0 and P_B and the state A' is specified by T_{A'} = 0 and P_A, then

\[ S_{A'}^o - S_{B'}^o < \Gamma_B > 0. \]

But \( \Gamma_A \) and \( \Gamma_B \) can be as small as we like by allowing \( T_A \) and \( T_{A'} \) to go to zero. Therefore

\[ |S_{B}^o - S_{A}^o| < \epsilon \]

where \( \epsilon \) is arbitrarily small. Equation (11) implies that

\[ S_{A'}^o = S_{B'}^o \]

which is the Nernst Heat Theorem.

Hence, the Nernst Theorem and the statement of unattainability are equivalent.

Isotherms and Adiabats

In Figure 1, AC is a reversible adiabatic path which is intersected by the reversible isotherms BD and B'D'. We ask whether we can draw an adiabatic path from A to B. If heat is absorbed in going along the isotherms in the cycle ABAC, the net result would be the conversion of heat into work without transferring any heat from a higher to a lower temperature. This is contrary to Kelvin’s principle. Thus, all points to the left of the reversible adiabat through A are inaccessible by adiabatic paths from A. On the other hand, if heat is absorbed along the isotherms in going from right to left, all points to the right of A would be inaccessible by adiabatic paths from A.

However, if the isotherm BC was an adiabat, the cycle ABCA would produce no work and absorb no heat. In all isotherms intersecting the adiabat AC between A and C were adiabats, Kelvin’s principle could not be used to find regions of states which were inaccessible from A along adiabats; Carnot’s principle would not be true; and the mathematical statement of the second law would not follow from the physical statements. Thus, it is important to prove that there are no regions in which isotherms are adiabats.

Assume that BC and B'C' are adiabatic isotherms. Then both the change in internal energy, \( \Delta E \), and heat, Q, are zero for the path B'B'C'C'. Hence, the First

\[ ^4 \text{Kelvin's principle states: In a cycle of processes, it is impossible to transfer heat from a heat reservoir and convert it all into work, without at the same time transferring a certain amount of heat from a hotter to a colder body.} \]

\[ ^4 \text{Carnot's principle states: From an arbitrary point (state), there is a finite region (set of states of finite measure) which cannot be reached by an adiabatic process, reversible or irreversible. This region may be taken arbitrarily near the initial point.} \]
Law tells us that the projection of this path onto the $p$-$v$ plane must have zero area. This constraint can be satisfied in one of three ways (Fig. 2a, b, and c). Figures 2a and 2b do not satisfy the conditions of the problem. Since we are considering a region in $p$-$v$-$T$ space, the zero area constraint must be satisfied for any adiabat and isotherm in that region. But the integrated area in Figure 2a is not zero for some isotherm $C^*B^*$; and it is not zero in Figure 2b for some reversible adiabat $DE$. Hence, only Figure 2c need be considered.

In thermodynamics it is assumed that in a one-component system, the specification of two independent intensive variables (say $p$ and $v$) completely determines any third variable (say $T$). The intersection of $BC$ and $B'C'$ on the $p$-$v$ plane violates this assumption. Therefore if the initial assumption is true the isotherms $BC$ and $B'C'$ cannot be adiabats, since being adiabats implies their intersection on the $p$-$v$ plane. Hence, in no region can isotherms be adiabats. This proof also applies to Figures 2a and 2b.

It is important to note that this proof hinges on the assertion that $p$ and $v$ are independent variables. Suppose we find a substance whose equation of state has $p$ as a function of $v$ alone, $p = p(v)$. In this case Figure 2c is not excluded and hence, it is possible for isotherms to be adiabats if $p = p(v)$. For such a substance the mathematical statement of the Second Law does not hold.