On the unattainability of absolute zero temperature and the Nernst heat theorem

Koun Shirai

Nanoscience and Nanotechnology Center, ISIR, Osaka University,
8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

Abstract

It is sometimes argued that the unattainability of zero temperature is a consequence of the second law of thermodynamics. Historically, the independence of the unattainability of zero temperature from the second law was proven more than 80 years ago, yet this assertion was repeated in the literature. This assertion naturally leads to a doubt that the unattainability of zero temperature is not equivalent to the Nernst heat theorem. The apparent contradiction between the Nernst heat theorem and residual entropy further complicates the problems of the third law. Totally, the validity of the third law seems to lose, giving an impression of somewhat ambiguous hypothesis to it. The author has recently settled the apparent contradiction between residual entropy and the Nernst heat theorem by refining the statement of the third law. Based on this refinement, two controversial problems, the independence of the unattainability of zero temperature from the second law and the equivalence of the unattainability with the Nernst heat theorem, have been solved.

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INTRODUCTION

Although it was established more than 80 years ago, it is strange to find that, even now, the third law of thermodynamics is subject to controversy. The problems of the third law in the early days are well described, for example, by Beattie and Oppenheim [1]. One of the reason for the controversy lies on the manner of the expression. The law is often stated as

**Third law: Expression (I)** The entropy of any system vanishes as temperature approaches zero.

This is called the Nernst (heat) theorem, although the original expression given by Nernst was slightly different ([2], p. 277). However, there are many exceptions for Expression (I) due to residual entropies. Glass materials and random alloys are known to have residual entropies. With the progress of material sciences, further exceptions are being found. Exceptions are no longer exception, which render the validity of the third law being restrictive.

There are other types of problem for the third law. The third law can be restated as

**Third law: Expression (II)** It is impossible to reach absolute zero temperature.

This expression is called the unattainability of absolute zero temperature [3]. In this case, there is no exception. The contrasting characters of the two expressions naturally arouse a doubt that the two expressions are not equivalent [4–11]. Hasse gave a thorough analysis of the relations between the Nernst theorem and the unattainability of zero temperature, but after all he gave the conclusions in a case-by-case manner [5]. Some authors argued that Expression (II) is a consequence of the second law of thermodynamics.

*(Statement 1)* The unattainability of zero temperature is deduced from the second law.

Simon criticized Statement 1 by analyzing the arguments of other authors [12]. Notwithstanding, objections such as Statement 1 appeared repeatedly in disguised forms. The problem of residual entropy further complicates the above questions.

Recently, the author has settled the problem of residual entropy by refining the expression of the third law. By defining the internal constraints accurately, he found a quantitative expression for the third law while acknowledging the existence of residual entropy. This paper is referred to as Paper (I). Now that the problem of residual entropy has been resolved, we are able to address other problems. In this paper, two controversial issues are solved from
the modern viewpoint made in Paper (I). First one is the independence of Expression (II) from the second law. The second one is the equivalence of Expression (II) with (I). Although a basic proof was given a long time ago by Simon [13] (see also Fowler and Guggenheim [14]), it is needed to improve the previous methods of proof while considering the problem of residual entropy. The readers are highly encouraged to read Paper (I).

INDEPENDENCE OF THE SECOND LAW

Second law The first issue to be discussed is the independence of the unattainability of zero temperature from the second law. The main logic underlying Statement 1 is based on the efficiency of the Carnot cycle \( \eta_C = 1 - T_l/T_h \), where \( T_h \) and \( T_l \) are the temperatures of the hot and cold heat reservoirs, respectively. When \( T_l = 0 \), the efficiency \( \eta_C \) becomes unity. This is equivalent to claim that the heat received from the hot reservoir can be completely transferred to work. With this result, it is claimed that reaching zero temperature contradicts the second law. The second law is sometimes stated in a brief form as

(Statement 2) Perfect conversion of heat to work is impossible.

The problem may be rooted in this brief expression of the second law, which prevails over many people’s mind without care. As a matter of fact, we can completely convert heat to work. For example, an isothermal expansion of an ideal gas in a cylinder does. Statement 2 must be replaced with a correct one,

The Second Law: There is no heat engine that can perform a complete conversion of heat to work.

The author apologizes to write such an easy matter in an original paper, but it is worth emphasizing here, because many erroneous assertions after all originate from this.

Let us analyze the problem behind Statement 2. Suppose that an ideal gas fills a cylinder with the initial volume \( V_1 \), contacting a low-temperature heat reservoir at \( T_l \). Let the entropy of the initial state of the gas be \( S_1 \). Assume that all the processes are performed in a reversible manner. On contacting a high-temperature heat reservoir at \( T_h \), the heat received by the gas can be completely transmitted to an external device in a work form. As a result, the volume of the gas is increased to \( V_2 \) and the entropy is increased to \( S_2 \). Unfortunately, this process alone is not usable for continuous operations, for the obvious reason that the
ever-expanding cylinder cannot be equipped in cars. Heat cycle is needed. The working gas must be returned to the initial state of unexpanded volume $V_1$ at the low temperature $T_1$. Therefore, the necessity of the recovery of the initial state precedes the necessity of heat rejection. The latter is merely a means for achieving the former. When $T_l = 0$, we can restore the original state $V_1$ in an isothermal process without rejecting heat, because $Q = T_l \Delta S$ vanishes for any change in entropy $\Delta S$. There is no conflict with the second law. This was figured out a long time ago [15, 16]. Nonetheless, Statement 2 is so appealing that we may be vulnerable to this statement without care.

**Significance of heat engines** We have to ask why we stick to the Carnot engine for obtaining zero temperature. The impossibility of the operation of the Carnot engine with $T_l = 0$ is correct, but this merely states that the engine is incapable of operating with the low-temperature reserver at $T = 0$. Maintaining is different from reaching there.

A similar argument holds for the Carnot refrigerator to obtain the zero temperature [10]. It is correct to state that zero temperature cannot be reached by any refrigerator, how idealized it is. Again, a heat cycle is not necessary for reaching zero temperature, and the use of heat cycle makes the problem even worse. A Carnot refrigerator, by construction, assumes that it is able to cool down adiabatically the working substance to the temperature of the cold reserver. If zero temperature is reachable in this step, no further step of the cycle is required. A single path is the best choice: cycles need to pay a price.

**PATH TO ZERO TEMPERATURE AND IRREVERSIBILITY**

The second issue is the equivalence of Expression (I) to Expression (II). The author believes that the debates on the equivalence of Expression (I) and (II) ended in the 1940s with a conclusion confirming the equivalence [12]. Despite this, the issue is still controversy in the physics community. The reason why this is so confusing lies mainly on the treatment of residual entropy. Let us discuss the equivalence in the order from easy to difficult.

**Reversible path** We have seen in the foregoing argument that the use of a single adiabatic path is the best choice for obtaining the zero temperature [17]. A proof of the unattainability of zero temperature will be, therefore, completed by showing that there is no adiabatic path to reach $T = 0$. Indeed, this is what Fowler and Guggenheim did in their textbook [14]. Here, the author first follows their method for developing theory further.
of adiabatic accessibility \[18\] is used, the proof is completed by a few lines of text \[19\]. Nevertheless, the method of Fowler and Guggenheim has a merit in the present context, which will be clearer later.

The best adiabatic processes are reversible ones in terms of the best efficiency. Figure

![Diagram](image)

**FIG. 1:** Temperature-entropy diagram for obtaining zero temperature. (a) Entropies along paths of a constant \(X\) all must converge to a single point. (b) For the case of residual entropy between two systems \(A\) and \(B\), there is a region inhibited from both systems (hatched region).

\[ S_\alpha(T) = S_\alpha(0) + \int_0^T \frac{C_X(T')}{T'} dT'. \]  
\[ S_\beta(T) = S_\beta(0) + \int_0^T \frac{C_\beta(T')}{T'} dT'. \]  
\[ S_\alpha(0) + \int_0^{T_1} \frac{C_\alpha(T')}{T'} dT' = S_\beta(0) + \int_0^{T_2} \frac{C_\beta(T')}{T'} dT'. \]

Suppose that we can reach \(T_2 = 0\). Then, we must have

\[ S_\beta(0) - S_\alpha(0) = \int_0^{T_1} \frac{C_\alpha(T')}{T'} dT'. \]
If $S_{\beta}(0) > S_{\alpha}(0)$, we can always find the nonzero solution for $T_1$ in Eq. (3), because specific heat is always positive. This result contradicts the unattainability of zero temperature. Hence, it must be $S_{\beta}(0) \leq S_{\alpha}(0)$. Now, we can start from a state $1'$ on $X = \beta$ such that $S_{\beta}(1') > S_{\alpha}(0)$, and bring the state towards $2'$ on $X = \beta$ by a reversible adiabatic path. A similar argument leads to $S_{\beta}(0) \geq S_{\alpha}(0)$. These two results lead to only a solution $S_{\beta}(0) = S_{\alpha}(0)$ which can be allowed.

Conversely, if $S_{\beta}(0) = S_{\alpha}(0)$ holds, there should be no reversible adiabatic path $\alpha \to \beta$ from a finite $T_1$ to $T_2 = 0$. For if a path $\alpha(T_1) \to \beta(T_2)$ exists, then Eq. (2) would lead to a finite $T_1$ satisfying

$$S_{\beta}(0) - S_{\alpha}(0) = \int_0^{T_1} \frac{C_{\alpha}(T')}{T'} dT'. \quad (4)$$

This contradicts the initial assumption $S_{\beta}(0) = S_{\alpha}(0)$, because the right-hand side of Eq. (4) is positive. Thus, we have proven the equivalence between Expressions (I) and (II). Similar proofs, but essentially equivalent, are seen in the literatures [16, 20–22].

Readers may be concerned, in Fig. 1(a), that there is a region wherein no isentropic path connecting $\alpha$ and $\beta$ exists, e.g., an isentropic path starting from state $1''$ on $X = \alpha$ to any state on $X = \beta$. However, it is physically sound to assume that there is continuity in the states of $A$ between $\alpha$ and $\beta$. We can always find a constant line $X = \beta'$, which has the intersection $2''$ between the isentropic path starting from $1''$ and a line $X = \beta'$.

Irreversible path There is an objection to the above argument. Hasse claims that the above proof using both ways of discrimination, $S_{\beta}(0) \leq S_{\alpha}(0)$ and $S_{\beta}(0) \geq S_{\alpha}(0)$, does not hold when an irreversible path is considered [5]. Let us consider an irreversible adiabatic path starting, for example, from 3 on $X = \alpha$ of Fig. 1(a). Suppose that, at $T = 0$, there is such a state $4'$ on a curve $X = \beta'$ whose entropy is larger than $S_{\alpha}(0)$. The transition $3 \to 4'$ does not conflict with the second law. The problem of his argument is that it misses the fact that the adiabatic process ceases at some point $T_4$ between $T_3$ and $T = 0$, because the temperature that can be reached by irreversible processes starting from a given state is always higher than the temperature that would be reached by the reversible process starting from the same state. This shows directly the unattainability of zero temperature: the above proof by the both ways of discrimination is unnecessary. The arguments hitherto discussed were already given by Fowler and Guggenheim [14] and others.

Case of residual entropy Now, we are in a position to discuss the special case of irreversible processes in which residual entropy is involved. In this case, there indeed exists a
state having a finite entropy at \( T = 0 \), as shown in Fig. 1(b). In a review paper by Landsberg, by using a similar figure, while claiming that the unattainability of zero temperature holds within each of branches \( A \) and \( B \), he reserved judgement about the transition between \( A \) and \( B \) [8]. Hatsopoulos and Keenan claimed that there is no proof that excludes the possibility of an irreversible adiabatic process of this type ([4], p. 29 in Forward).

As discussed in paper (I), a residual entropy arises between two systems that are separated by a special internal constraint expressed by a frozen coordinate. In the thermodynamic context given by Gyftopoulos and Beretta [23], even for the same material, if two states have different internal constraints, we have to regard two “states” as different systems. For example, ice crystals having ordered and disordered structures belong to different systems, despite consisting of the same water molecules.

Figure 1(b) shows a \( T - S \) diagram of systems \( A \) and \( B \) when a residual entropy is present between them. Two systems \( A \) and \( B \) are separated by a frozen coordinate \( r \); they are called belonging to different thermodynamic classes in Paper (I). The value is fixed at \( \hat{r}_A \) for \( A \) and at \( \hat{r}_B \) for \( B \), leaving a finite difference \( \Delta \hat{r}_{AB} = \hat{r}_B - \hat{r}_A \). Since, by an appropriate transformation, the total entropy can be factorized as \( S = \sum_j s_j(q_j) \) (Eq. 7 in Paper I), it is permissible to use a simple functional form \( S(T, \hat{r}) \) in the following argument. Let us assume \( S_B(0, \hat{r}_B) > S_A(0, \hat{r}_A) \). We are considering an adiabatic transition \( A \rightarrow B \) starting from a state \( A_1 \) of system \( A \) at a nonzero \( T_1 \), whose entropy \( S_A(T_1, \hat{r}_A) \) is less than \( S_B(0, \hat{r}_B) \), and asking the possibility of reaching \( T = 0 \) in system \( B \).

A transition from \( S_A(T_1, \hat{r}_A) \) to \( S_B(0, \hat{r}_B) \) is compatible with the second law, because of increase in \( S \). However, the internal constraint strictly restricts the accessible regions \( (T, S) \). The region allowed for \( A \) is disconnected from the region allowed for \( B \), as indicated by the hatched area in Fig. 1(b). In terms of the frozen coordinate \( r \), the shaded area corresponds to a range of \( r \) from \( \hat{r}_A \) to \( \hat{r}_B \). The adiabatic process starting from \( A_1 \) proceeds until reaching a state \( A_2 \) at the boundary of \( A \). At this point, the internal constraint is removed. Then, the frozen coordinate \( \hat{r} \) becomes a real variable \( r \). The system does change from \( A \) to \( B \). Since, during changing of \( r \) from \( \hat{r}_A \) to \( \hat{r}_B \), the system is in nonequilibrium, the entropy jumps by \( \Delta S^{AB}(T_2) = S_B(T_2, \hat{r}_B) - S_A(T_2, \hat{r}_A) \). Here, \( T \) is assumed to be constant. Usually in solids, the temperature increases, \( T_2' > T_2 \), except a negligible decrease due to the volume expansion if presents (see Appendix). The constant \( T \) is, therefore, the best case. At the end point \( B_2' \), system \( B \) attains an entropy value \( S_B(2') \), which is larger than
From $B_2$, there is no adiabatic path to the lowest-entropy state $B_0$, as is evident from Fig 1(b). Therefore, we cannot reach $B_0$ from $A_1$ all the more. The residual entropy $S_{0}^{AB}$ is the limiting value of the discontinuity $\Delta S^{AB}(T_2)$ as $T_2 \to 0$.

The above argument of proof is instructive for understanding of the accessibility of thermodynamic states. Reversible processes are certainly the processes retaining a constant entropy, $\Delta S_{12} = 0$. However, the converse is not always true. When the end states 1 and 2 are separated by an internal constraint, we cannot find adiabatic paths with a constant $S$ from 1 to 2. On the way from 1 to 2, an entropy jump occurs. The origin of entropy has been changed. In this way, judging the accessibility by comparing only the end states is risky.

There are confusing descriptions in the literature. Wilks ascribed the impossibility of reaching zero temperature when residual entropy exists to the impossibility of changing frozen-in states by external parameter ([22], p. 115). This is not true. As described in Paper (I), there must be at least one reversible path for any transition $A \to B$, and this is so even when the transition is caused by removing the internal constraint. Removing the internal constraint alone is irreversible. However, if we bring another system $C$, and make a thermal contact to the combined system $A + B$, we will find a reversible path. In fact, the measurement of residual entropy $S_{0}^{AB}$ is carried out in this way. However, the fact of the increase in entropy from $S_A(2)$ to $S_B(2')$ does no change, because entropy is a state variable. By replacing the irreversible path $2 \to 2'$ with a reversible one, the increase $\Delta S^{AB}(T_2)$ must be compensated with a decrease in entropy of $C$. This means that heat is injected to $A$, and therefore it is not usable for cooling.

When looking at specific problems of condensed matters, we find many unsolved or tricky arguments on the third law, for which deep knowledge of individual materials is required. These topics spread from ideal gases [24], Bose-Einstein gases [25–27], quantum cooling, [28, 31], and even to black holes [32]. Before going to individual problems, we have to know exactly what is the third law. This paper gives general feature of the third law from the macroscopic viewpoint.

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Appendix

In this appendex, we show that, when the internal constraint is adiabatically removed from system $A$ (the process $2 \rightarrow 2'$ in Fig. II(b)), the temperature of $A$ is increased or at best constant. In the following, we show this by separately treating the cases in the relationships between the internal energies $U_A(2)$ and $U_B(2')$. All the reference numbers for figures and Examples are those of Paper I.

Case 1, $U_B(2') > U_A(2)$

This is the case of Example 6 of creating defects in silicon by an electron irradiation. Interstitial atoms are in excited states with the total energy increase by $\Delta U_I$. Introducing $n_I$ interstitial atoms among $N_I$ available interstitial sites yields an entropy increase $\Delta S_{\text{dis}} = \ln(N_I/n_I)$. Although system $A$ adiabatically increases the entropy $S_A$ by $\Delta S_{\text{dis}}$, the process does not occur until mechanical work $W$ is supplied in order to increase the total energy by $\Delta U_I$. This $W$ must come from the energy transfer from the incident electron beam. The best case is the perfect energy transfer $W = \Delta U_I$. As in Example 2, if we grasp perfectly atom positions, and if we can move each atom to the intended position exactly, the entropy change $\Delta S$ must be 0 but not $\Delta S_{\text{dis}}$. However, this occurs only for the case of head-on collision. Only a tiny incline of the incident beam causes a chain of uncontrollable collisions. Most part of the supplied mechanical work is dissipated into a heat generation $Q_{\text{gen}}$. Accordingly, $\Delta U_I = W - Q_{\text{gen}}$, and the total entropy is further increased by $Q_{\text{gen}}/T_2$. This results in an increase in $T_2'$.

Case 2, $U_B(2') = U_A(2)$

This is the case of Example 5 of formation a random alloy $XY$. Here, $A$ is the separated system $(X|Y)$ and $B$ is the mixed system $(XY)$. In this case, no external work is necessary. The natural process occurring at a finite temperature $T_2$ is intermixing of $X$ and $Y$. There is no reason for decreasing in $T$.

Case 3, $U_B(2') < U_A(2)$

A rare case is that a disordered system $B$ has a lower energy than the ordered system $A$. The present theory does treat even this case (see Sec. III B of Paper I), although traditional theories exclude it. Because the process is adiabatic, the decrease in $U$ turns to an internal generation of heat $Q$. The decrease in $T$ never takes place.
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