Relationship of thermoelectricity to electronic entropy

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It is shown that S_X, the partial molal entropy of electrons in material X, is given by $S_X = -F\alpha_X$, where F is Faraday's constant and α_X the absolute thermoelectric power of X. This result depends on three propositions. (1) The Kelvin relations are valid for all thermoelectric materials. (2) Under isothermal conditions, the Peltier effect is truly reversible. (3) For a degenerate free-electron Fermi gas, the thermoelectric power is proportional to the entropy.

INTRODUCTION

It has been 130 years since Thomson (Lord Kelvin) established the fundamental equations relating the Seebeck effect, the Peltier effect, and the Thomson effect.[1] The equations for an isotropic substance are usually expressed in the form

$$\mu = T\frac{d\alpha}{dT} , \tag{1}$$

$$\Pi = T\alpha , \tag{2}$$

where μ is the Thomson coefficient, Π is the Peltier coefficient, and α is usually called the absolute thermoelectric power, though a better term would be the absolute Seebeck coefficient. (We use the symbol α for thermoelectric power rather than the more commonly used symbol S in order to reserve S to symbolize entropy.)

The quantities μ and α are expressed in units of volts or microvolts per degree Kelvin. They can be formally converted to quantities having the units of specific heat or entropy by multiplying by electric charge. We will assume throughout this paper that electrons are the charge carriers. Thomson suggested that μ (multiplied by charge, of course) might be regarded as the specific heat of electricity of the material. An equivalent proposition is that α is the electronic entropy divided by the charge of the electron. This idea has been a point of controversy for many years.[2] The crux of the problem is that Thomson coefficients can only be measured in materials in which a temperature gradient exists at the time of the measurement. Thus, Thomson coefficients cannot be measured under truly reversible conditions. The quantity α is obtained from μ by integration

$$\alpha = \int_0^T \frac{\mu}{T}dT . \tag{3}$$

Consequently, authors in the field are careful to point out that the thermoelectric power multiplied by the charge of the electron is to be regarded as a "transport entropy" which is not necessarily equal to the "static entropy" of the electrons in the material under isothermal conditions.[2,3] It is the purpose of this paper to examine the question of whether it might be generally true that the thermoelectric power equals the electronic entropy divided by the charge of the electron.

THEORETICAL DEVELOPMENT

We begin by assuming that the Kelvin relations are valid for all thermoelectric materials. From the Kelvin relations, the reversible Peltier heat associated with the passage of a mole of electrons from material A to material B:

$$e_{(A)}^- \rightarrow e_{(B)}^- \tag{4}$$

is given by

$$Q_{\text{rev}} = -F\Pi_{BA} = -F(\alpha_B - \alpha_A)T , \tag{5}$$

where F is Faraday's constant, and the negative sign accounts for the negative charge of the electron. In contrast to the Thomson effect, the Peltier effect can be observed under truly reversible conditions by holding both junctions of a thermocouple at the same temperature to eliminate Fourier heat conduction, and by moving electrons around the circuit very slowly to eliminate Joule heating. The reversible heat transferred under these conditions depends on the properties of pairs of materials A and B, so a Peltier experiment cannot be used to find absolute thermoelectric powers of individual materials. However, because the process takes place under truly reversible conditions, the entropy of reaction ΔS is

$$\Delta S = (S_B - S_A) = \frac{Q_{\text{rev}}}{T} = -(\alpha_B - \alpha_A)F . \tag{6}$$

The symbols S_A and S_B are to be interpreted as *partial molal* entropies of electrons in materials A and B, respectively, to allow for the possibility that electrons may interact strongly with the lattice. Equation (6) can only be true, in general, if the following relation is true:

$$S_X = -\alpha_X F + C(T) \tag{7}$$

for all materials X. The function $C(T)$ is a universal function which may depend on the temperature, but not on the material. One immediately concludes that $C = 0$ at $T = 0$ K because thermoelectric powers and entropies are both 0 at 0 K.

In order to evaluate $C(T)$ at other temperatures, we introduce the concept of an ideal thermoelectric material. This is a material which has the properties that (1) the Kelvin relations are valid, and (2) the electrons have the static and transport properties of a degenerate free-electron Fermi gas. It is well known that for a degenerate free-electron Fermi gas, the thermoelectic power is related to the entropy by[4]

$$S_I = -AF\alpha_I . \tag{8}$$

The subscript I refers to "ideal." The value of A depends on the assumptions that are made about the relaxation time

and mean free path of the electrons. For our purposes, it is the functional form of Eq. (8) which is important.

Equations (7) and (8) can be simultaneously satisfied only if

$$A = 1 \ , \tag{9}$$

$$C(T) = 0 \ . \tag{10}$$

Since $C(T)$ is a universal function for all materials obeying the Kelvin relations, we have the desired general result.

$$S_X = -\alpha_X F \ . \tag{11}$$

Material X need not be an ideal thermoelectric material.

DISCUSSION

This result depends on three premises: (1) The Kelvin relations are valid. (2) The Peltier effect can be observed under isothermal, hence reversible conditions. (3) Equation (8) gives the correct functional form of the relationship between the thermoelectric power and the entropy of a degenerate free-electron Fermi gas. The last premise is probably the only one which can be seriously questioned, and then only by accepting the unpleasant conclusion that contemporary theory would be unable to predict even the correct functional form of the thermoelectric power for the simplest of idealized systems. Such a conclusion seems un-

likely, and Eq. (8) seems to be generally accepted at the present time.

Equation (11) shows that "nonideal" effects such as the so-called phonon-drag effect[5] contribute to the static partial molal entropy of the electrons and are not exclusively associated with the transport entropy of a flow of charge carriers under irreversible conditions. Therefore, the phonon-drag effect and other possible nonideal effects are present in isothermal specimens of metals as well as in specimens in which a thermal gradient exists. Obviously, when such effects become important, the electrons can no longer be treated as a quasi-isolated system separate from the lattice. In such cases of interacting systems, it is appropriate to use partial molal thermodynamic quantities in describing the composite system. The use of partial molal quantities has long been practiced in classical solution thermodynamics, but this approach seems to have been little used in the study of thermoelectricity.

Apart from its relationship to the theory of thermoelectricity, the results of Eq. (11) may be of more general scientific interest. They provide probably the only practical and generally valid method by which to obtain partial molal entropies of electrons in metals.

ACKNOWLEDGMENTS

[1]William Thomson, first Baron Kelvin, *Mathematical Physical Papers* (Cambridge Press, 1882), Vol. 1, pp. 232–291 [Trans. R. Soc. Edinburgh, Vol. XXI, Pt. I, read 1 May 1854].

[2]For a brief review, see F. J. Blatt, P. A. Schroeder, C. L. Foiles, and D. Greig, *Thermoelectric Power of Metals* (Plenum, New York, 1976), pp. 164–167.

[3]D. K. C. MacDonald, *Thermoelectricity: An Introduction to the Principles* (Wiley, New York, 1962), pp. 9–11; C. A. Domenicali, Rev. Mod. Phys. **26**, 238 (1954).

[4]MacDonald, Ref. 3, pp. 25, 46; J. M. Ziman, *Principles of the Theory of Solids* (Cambridge Univ. Press, London, 1964), pp. 202, 203.

[5]Blatt *et al.*, Ref. 2, p. 87.