

THE THERMOELECTRIC PROCESS

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ABSTRACT

The efficiency of thermoelectric technology today is limited by the properties of available thermoelectric materials and a wide variety of new approaches to developing better materials have recently been suggested. The key goal is to find a material with a large ZT, the dimensionless thermoelectric figure of merit. However, if an analogy is drawn between thermoelectric technology and gas-cycle engines then selecting different materials for the thermoelements is analogous to selecting a different working gas for the mechanical engine. And an attempt to improve ZT is analogous to an attempt to improve certain thermodynamic properties of the working-gas. An alternative approach is to focus on the thermoelectric process itself (rather than on ZT), which is analogous to considering alternate cycles such as Stirling vs. Brayton vs. Rankine etc., rather than 'merely' considering alternative 'gases'. Focusing on the process is a radically different approach compared to previous studies focusing on ZT. Aspects of the thermoelectric process and alternative approaches to efficient thermoelectric conversion are discussed.

INTRODUCTION

Modern thermoelectric energy conversion devices achieve only a small fraction of Carnot efficiency. The fundamental problem is that the transport properties of available materials are insufficient. In spite of significant effort, neither the experimental nor the theoretical situation has changed substantially in several decades [1].

Experimentally, there are several rather different thermoelectric materials available which achieve about the same efficiency over different temperature ranges (approximate peak efficiency temperatures shown in parenthesis): BiSb alloys (100 K), Bi₂Te₃-based alloys (300-400 K), PbTe-based alloys (600 K-700 K), and SiGe alloys (1100-1200 K). The best thermoelectric materials each achieve peak efficiency values up to about 17% of Carnot efficiency. Moreover, it is not simply the case that more efficient materials are known but are impractical for some reason. There simply aren't any known materials with significantly better thermoelectric properties.

Theoretically, however, there is no known upper limit to the efficiency of thermoelectric conversion beyond the usual Carnot limit. A natural question is, then: why do the best known thermoelectric materials exhibit about the same, relatively low efficiency?

Rather than focusing on the properties of individual thermoelectric materials, this paper attempts to illuminate the question by examining the nature of the thermoelectric conversion process itself. It is shown that an analogy can be drawn between the thermoelectric conversion process and a type of thermodynamic process involving exchange of particles which, it turns out, exhibits many features usually associated with thermoelectric processes.

The following sections outline the essential phenomenology of thermoelectricity and using a parallel formalism a particular open thermodynamic process. Based on this analogy, the 'thermoelectric cycle' can be described. A more familiar example, based on a conventional pressure-volume-temperature (P - V - T) is also described in a similar way. Some typical

experimental results and resulting efficiencies are briefly discussed and finally, some conclusions are presented.

THERMOELECTRICITY

Thermoelectricity may be characterized by the simultaneous effects of both electrical and thermal currents. Using the conventional definitions for the transport coefficients, thermoelectric behavior is well approximated by

$$\begin{aligned}\vec{i} &= \sigma_T (\vec{E} - \alpha \vec{\nabla} T) \\ \vec{q} &= T \vec{s} \\ &= \alpha T \vec{i} - \lambda_T \vec{\nabla} T\end{aligned}\quad (1)$$

or

$$\begin{pmatrix} \vec{i} \\ \vec{s} \end{pmatrix} = L \begin{pmatrix} \vec{E} \\ -\vec{\nabla} T \end{pmatrix}\quad (2)$$

with the transport matrix L given by

$$L = \begin{pmatrix} \sigma_T & \sigma_T \alpha \\ \sigma_T \alpha & \lambda_T / T \end{pmatrix}\quad (3)$$

Here i is the electric current density, E is the electric field, q is the heat current density, s is the entropy current, ∇T is the temperature gradient, σ_T is the electrical conductivity and α is the Seebeck coefficient. λ_E is the thermal conductivity measured under the condition of zero electric field. The symmetry of Eq. (3) (i.e. that the off diagonal elements of the coefficient matrix are identical) is due to one of the Onsager reciprocal relations [2].

Because measurement of thermal conductivity under the condition $E=0$ presents experimental difficulties, the ordinary thermal conductivity (λ_i) is measured under the condition $i=0$. Similarly, the electrical conductivity may be measured in more than one way. The ordinary electrical conductivity (σ_T) is measured with zero temperature gradient. In principle, however, the electrical conductivity could also be measured under adiabatic conditions, that is with $q=0$. The adiabatic electrical conductivity (designated σ_q) is smaller than the isothermal electrical conductivity. Using the definitions and Eq. (3), the relationships between the thermal and electrical coefficients may be succinctly summarized by

$$\begin{aligned}\gamma_{Ei} &\equiv \frac{\lambda_E}{\lambda_i} \\ &= \frac{\sigma_T}{\sigma_q} \\ &= 1 + \frac{\sigma_T \alpha^2 T}{\lambda_i} \\ &\equiv 1 + ZT\end{aligned}\quad (4)$$

where ZT is the dimensionless thermoelectric figure of merit. The symbol γ is introduced here because of the similarity (which will be illustrated below) with the ratio of the constant pressure to constant volume specific heat.

THERMODYNAMICS OF AN OPEN, ONE COMPONENT SYSTEM

The thermodynamics of an open, one component system can be described using a notation similar in form to the notation used above for thermoelectricity. Consider a substance consisting of N particles characterized by a chemical potential μ and temperature T , each of which is allowed to vary. In particular, consider the thermodynamics of adding a particle to the system. The changes in N , heat and entropy are given by

$$\begin{aligned}
 dN &= \left. \frac{\partial N}{\partial \mu} \right|_T d\mu + \left. \frac{\partial N}{\partial T} \right|_{\mu} dT \\
 dQ &= TdS \\
 &= -\mu dN + dU \\
 &= -\left(\left. \frac{\partial U}{\partial N} \right|_T - \mu \right) dN + \left. \frac{\partial U}{\partial T} \right|_N dT
 \end{aligned} \tag{5}$$

which is conveniently summarized in matrix form as

$$\begin{pmatrix} dN \\ dS \end{pmatrix} = C \begin{pmatrix} d\mu \\ dT \end{pmatrix} \tag{6}$$

with the capacity matrix, C , given by

$$C = \begin{pmatrix} \left. \frac{\partial N}{\partial \mu} \right|_T & \left. \frac{\partial N}{\partial T} \right|_{\mu} \\ \frac{1}{T} \left. \frac{\partial N}{\partial \mu} \right|_T \left(\left. \frac{\partial U}{\partial N} \right|_T - \mu \right) & \frac{1}{T} \left[\left. \frac{\partial U}{\partial T} \right|_N + \left. \frac{\partial N}{\partial T} \right|_{\mu} \left(\left. \frac{\partial U}{\partial N} \right|_T - \mu \right) \right] \end{pmatrix} \tag{7}$$

The symmetry of C is a consequence of the second law of thermodynamics and the off-diagonal elements are exactly equal

$$\begin{aligned}
 C_{12} &= \left. \frac{\partial N}{\partial T} \right|_{\mu} \\
 &= C_{21} \\
 &= \frac{1}{T} \left. \frac{\partial N}{\partial \mu} \right|_T \left(\left. \frac{\partial U}{\partial N} \right|_T - \mu \right)
 \end{aligned} \tag{8}$$

C_{22} may be identified as the entropy capacity at constant μ (C_{μ}) and using Eqs. 7 and 8

$$\begin{aligned}
C_\mu &\equiv \frac{1}{T} \left. \frac{\partial \mathcal{U}}{\partial T} \right|_\mu \equiv C_{22} \\
&= \frac{1}{T} \left[\left. \frac{\partial \mathcal{U}}{\partial T} \right|_N + \left. \frac{\partial \mathcal{N}}{\partial T} \right|_\mu \left(\left. \frac{\partial \mathcal{U}}{\partial \mathcal{N}} \right|_T - \mu \right) \right] \\
&= \frac{1}{T} \left. \frac{\partial \mathcal{U}}{\partial T} \right|_N \left[1 + \frac{\left. \frac{\partial \mathcal{N}}{\partial \mu} \right|_T \left(\left. \frac{\partial \mathcal{U}}{\partial \mathcal{N}} \right|_T - \mu \right)^2}{\left. \frac{\partial \mathcal{U}}{\partial T} \right|_N} \right]
\end{aligned} \tag{9}$$

The prefactor of Eq. 9 is just the entropy capacity at constant N (C_N), and a γ can now be defined for this system as well

$$\begin{aligned}
\gamma_{\mu N} &= \frac{C_\mu}{C_N} \\
&= 1 + \frac{\left. \frac{\partial \mathcal{N}}{\partial \mu} \right|_T \left(\left. \frac{\partial \mathcal{U}}{\partial \mathcal{N}} \right|_T - \mu \right)^2}{\left. \frac{\partial \mathcal{U}}{\partial T} \right|_N}
\end{aligned} \tag{10}$$

At this point the structure of the capacity matrix C may not appear particularly similar to the structure of the transport coefficient matrix L , but the primary difference is that the coefficients of C are simply less familiar.

CONVERSION EFFICIENCY

Define the thermoelectric efficiency as

$$\mathcal{E}_{Ei} \equiv \frac{-\vec{E} \cdot \vec{i}}{\vec{s} \cdot (-\vec{\nabla} T)} \tag{11}$$

Using Eq. (1) to eliminate E and q , and optimizing with respect to i , the maximum efficiency can be derived for a fixed ∇T :

$$\mathcal{E}_{Ei}^{\max} = \frac{\sqrt{\gamma_{Ei}} - 1}{\sqrt{\gamma_{Ei}} + 1} \tag{12}$$

This is the usual expression for the efficiency of a thermoelectric generator, which approaches unity as γ_{Ei} (or ZT) diverges.

The analogous efficiency expression for the μ - N system is

$$\mathcal{E}_{\mu N} \equiv \frac{-d\mu dN}{dSdT} \tag{13}$$

$d\mu dN$ is simply the infinitesimal chemical (or electrochemical, if the particles are charged) work performed by a cyclical process of two constant chemical potential processes $d\mu$ apart and two constant particle number processes dN apart. This work is illustrated schematically in Fig. 1.

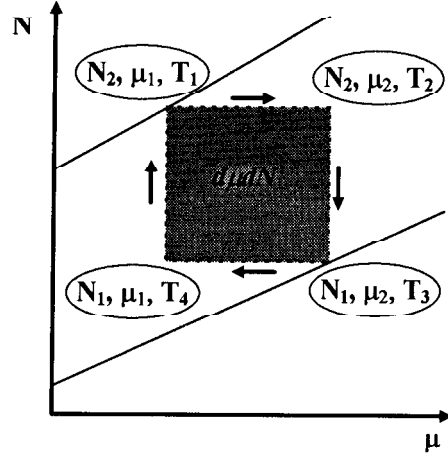


Fig. 1: Schematic representation of $d\mu dN$ work. The lines indicate the N - μ equation of state at T_1 and T_3 .

$dSdT$ represents the infinitesimal work performed by a cyclical process consisting of two isothermal steps dT apart and two adiabatic steps dS apart in entropy. The efficiency defined in Eq. (0) is, therefore, the ratio of the actual work performed in this type of process to the work performed by a Carnot cycle operating between two temperatures represented by dT .

The maximum efficiency for this type of process is derived in precise analogy to the thermoelectric expression above: use Eq. 7 to eliminate $d\mu$ and dS , and optimize with respect to dN

$$\epsilon_{\mu N}^{\max} = \frac{\sqrt{\gamma_{\mu N}} - 1}{\sqrt{\gamma_{\mu N}} + 1} \quad (14).$$

The similarity in form between the expression for the efficiency of this μ - N system and the thermoelectric system carries over to the magnitude of the efficiency also, which may

be illustrated by the following discussion.

As a specific example, consider a non-degenerate electron gas with the usual equation of state

$$N = 2.5 \times 10^{19} \left(\frac{T}{300} \right)^{1.5} e^{\mu/kT} \text{ cm}^{-3} \quad (15)$$

and internal energy

$$U = \frac{3}{2} NkT \quad (16)$$

from which we can calculate the capacity matrix

$$C = \frac{N}{kT} \begin{pmatrix} 1 & k \left[\frac{3}{2} - \frac{\mu}{kT} \right] \\ k \left[\frac{3}{2} - \frac{\mu}{kT} \right] & k^2 \left\{ \frac{3}{2} + \left[\frac{3}{2} - \frac{\mu}{kT} \right]^2 \right\} \end{pmatrix} \quad (17)$$

and the ratio of the entropy capacities

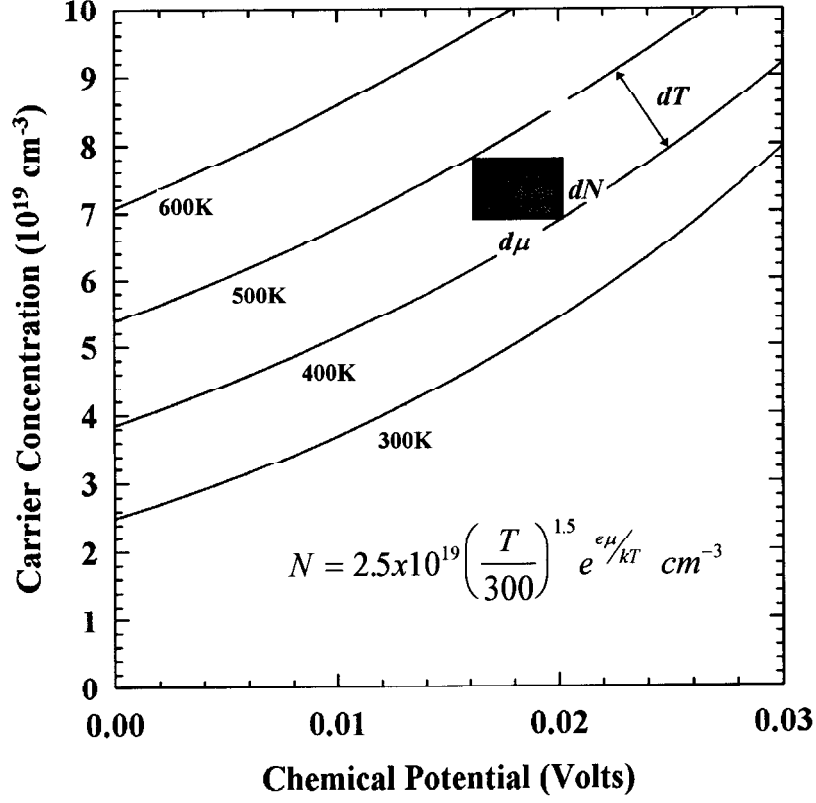


Fig. 2: Equation of state for a non-degenerate electron gas illustrating $d\mu dN$ work.

$$\gamma_{\mu N} = 1 + \frac{\left(\frac{3}{2} - \frac{\mu}{kT} \right)^2}{\frac{3}{2}} \quad (18)$$

If we further assume an energy independent mean free path and we neglect heat transport due to phonons, we can calculate the transport matrix

$$L = \sigma_T \begin{pmatrix} 1 & \frac{k}{e} \left[2 - \frac{\mu}{kT} \right] \\ \frac{k}{e} \left[2 - \frac{\mu}{kT} \right] & \left(\frac{k}{e} \right)^2 \left\{ 2 + \left[2 - \frac{\mu}{kT} \right]^2 \right\} \end{pmatrix} \quad (19)$$

and the ratio of the thermal conductivities

$$\gamma_{Ei} = 1 + ZT = 1 + \frac{\left(2 - \frac{\mu}{kT}\right)^2}{2} \quad (20)$$

which is the usual result for ZT under these conditions.

In this case the transport matrix is very similar to the capacity matrix, differing primarily by the introduction of a characteristic relaxation time (which enters into the isothermal electrical conductivity, σ_T) and a minor modification of the numerical coefficients (i.e. where “3/2” enters several coefficients in C , “2” enters in L). Properly accounting for genuine transport effects (primarily the energy dependence of the relaxation time) and heat loss mechanisms (primarily phonon transport) greatly complicate this comparison, but it may be of interest to note that the order of magnitude of thermoelectric effects can be understood as originating from these fundamental thermodynamic considerations.

THE ‘THERMOELECTRIC CYCLE’

This section describes the thermodynamic cycle by analogy to the μ - N system described above. While this system is obviously not identical to the thermoelectric process, it nevertheless appears to capture many of the features essential to understanding thermoelectric phenomena and deserves some attention for that reason.

Fig. 2 illustrates the equation of state and $d\mu dN$ -type work discussed above for a non-degenerate electron gas. Since the process is far removed from a Carnot-cycle (composed of two isotherms and two adiabats), the efficiency is low. Nevertheless, at very low carrier concentrations (i.e. large, negative values of μ), $\gamma_{\mu N}$ diverges and the efficiency approaches unity, as indicated by of Eqs. 18 and 14.

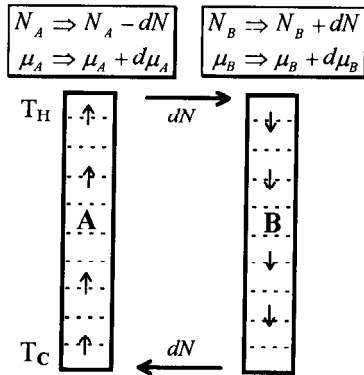


Fig. 3: The ‘thermoelectric cycle’ may be described as a succession of $d\mu dN$ processes, passing an infinitesimal charge (dN) around a closed circuit of dissimilar materials.

changes in a P - V system may be represented in an entirely similar way by

Fig. 3 illustrates how a conventional thermocouple may be thought of as a succession of infinitesimal $d\mu dN$ processes in which an infinitesimal charge dN circulates around the closed circuit. The work performed and efficiency of this process is surprisingly well described by entirely neglecting the true transport nature of the process and instead examining only the purely thermodynamic considerations described here, particularly if the effect of phonon transport is neglected.

THERMODYNAMICS OF A P - V SYSTEM

As a final example we consider a P - V system, which may be more familiar than the N - μ system above and where experimental data indicate at least one method for achieving high efficiencies. Using the ordinary thermodynamic definitions, state

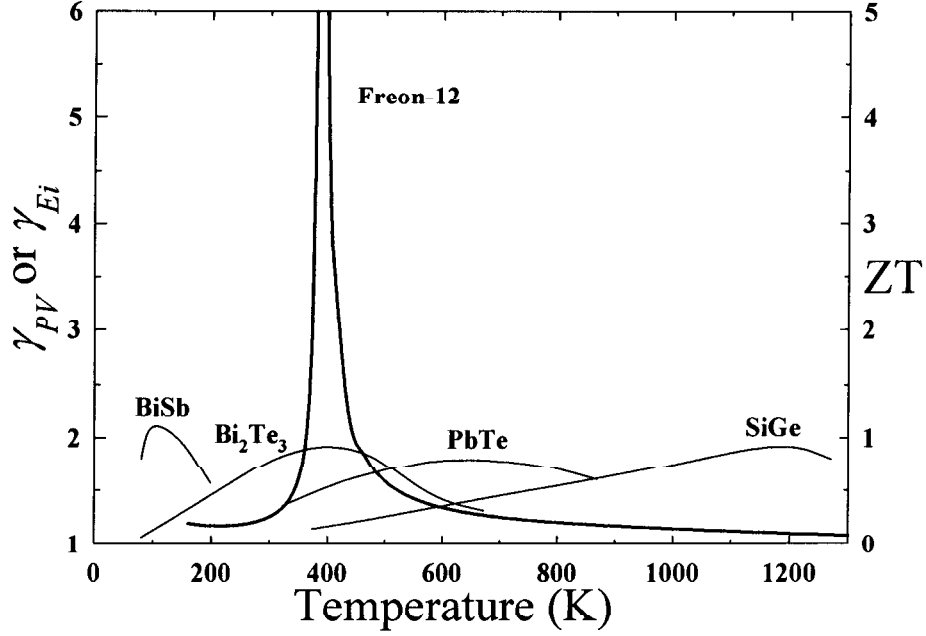


Fig. 4: Specific heat ratios, γ_{PV} for a PV system (Freon 12) and thermal conductivity ratios, $\gamma_{Ei}=1+ZT$, for selected n-type semiconductor alloys as a function of temperature.

$$\begin{pmatrix} dV \\ dS \end{pmatrix} = \begin{pmatrix} V\kappa_T & V\beta \\ V\beta & C_p/T \end{pmatrix} \begin{pmatrix} -dP \\ dT \end{pmatrix} \quad (21)$$

Here dV , dP , dS and dT have their usual thermodynamic meaning. κ_T is the isothermal compressibility, β is the volume coefficient of thermal expansion and C_p is the constant pressure specific heat. As above, the symmetry Eq. (21) (i.e. that the off diagonal elements of the coefficient matrix are identical) is a result of the well known Maxwell relations.

It is convenient to also define the constant volume specific heat (C_v) measured with $dV=0$ and the adiabatic compressibility (κ_S) measured with $dS=0$. The relationships between the heat capacities and compressibilities may be simply summarized by

$$\begin{aligned} \gamma_{PV} &= \frac{C_p}{C_v} \\ &= \frac{\kappa_T}{\kappa_S} \\ &= 1 + \frac{V\beta^2 T}{\kappa_T C_v} \end{aligned} \quad (22),$$

where now γ_{PV} has the conventional thermodynamic meaning.

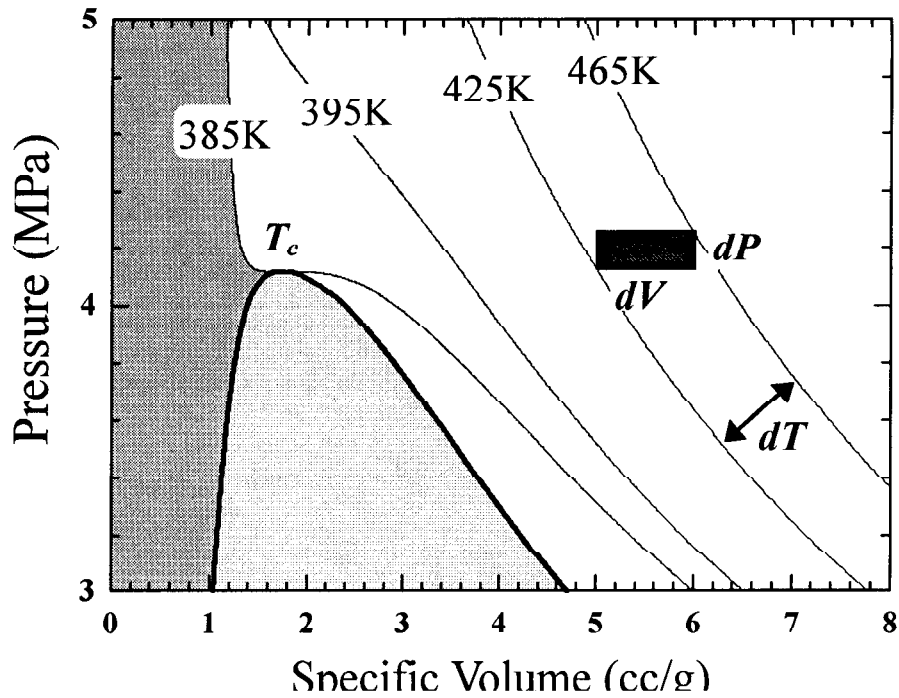


Fig. 5: PV diagram for Freon-12 (CCl_2F_2). The two phase region is light gray and the liquid is the darker gray region to the left. Isotherms are indicated by light lines and a typical $dPdV$ element is indicated by the rectangle.

TYPICAL EXPERIMENTAL RESULTS FOR THERMOELECTRICS

The thermoelectric figure of merit, ZT , has been measured for many materials and Fig. 4 shows representative results for three of the best n-type semiconductor alloys known. Even for the best known materials ZT does not yet significantly exceed unity, which is to say that γ_{Ei} does not significantly exceed 2.

TYPICAL RESULTS FOR GASES

For an ideal classical gas the equipartition theorem yields,

$$\gamma_{PV} = 1 + \frac{2}{f} \quad (23)$$

where f is the number of degrees of freedom associated with a single gas molecule. Since $f \geq 3$, $\gamma_{PV} < 1.67$ for ideal gases. At low pressures, for example, monatomic gases such as Argon exhibit $\gamma_{PV} \approx 1.67$.

Condensable gases, however, can exhibit values for γ_{PV} much greater than 2. As a typical example, the experimental properties of Freon 12 (calculated from fits given in [3]) have been used to illustrate the key features in Fig. 5.

Note that $\frac{\partial \mathcal{P}}{\partial \mathcal{V}_T} = 0$ at the critical temperature, T_c . Thus κ_T , C_P , and γ_{PV} all diverge at T_c . γ_{PV} of Freon 12 gas has been calculated from fits of the experimental results [3] for: $T < T_c$ along the boundary between the gas phase and the two phase region and for $T > T_c$ at the critical density (0.556 g/cm^3). The results are shown in Fig. 4 for comparison purposes.

Freon 12 has been chosen for illustrative purposes only and a great many other condensable gases exhibit qualitatively similar behavior: γ_{PV} is large for conditions near the critical point and approaches a value between 1 and 1.67 for conditions far from the critical point. The large values observed for γ_{PV} near the critical point are in sharp contrast to the universally small values of γ_{Ei} (less than about 2) reported for thermoelectric materials.

CONVERSION EFFICIENCY FOR THE ANALAGOUS P - V SYSTEM

The analogous efficiency expression for the P - V system is

$$\varepsilon_{PV} \equiv \frac{dP dV}{dS dT} \quad (24)$$

Interpretation is particularly simple for the PV system. $dP dV$ is simply the infinitesimal mechanical work performed by a cyclical process of two constant pressure steps dP apart and two constant volume steps dV apart. This work is illustrated by the small rectangle in Fig. 4.

Again, the maximum efficiency for this type of process is derived in precise analogy to the thermoelectric expression above (use Eq. 21 to eliminate dP and dS , and optimize with respect to dV):

$$\varepsilon_{PV}^{\max} = \frac{\sqrt{\gamma_{PV}} - 1}{\sqrt{\gamma_{PV}} + 1} \quad (25)$$

While γ_{PV} becomes very large for PV conditions near the critical point, under most conditions γ_{PV} is actually quite small. For example Freon 12, at 300 K and 0.1 MPa (1 atm.), has $\gamma_{PV} = 1.14$ and ε_{PV} of only 0.033 (i.e. 3.3% of Carnot efficiency).

It is important to point out that the familiar condensable gas conversions systems (such as Freon-based refrigerators and steam engines) are not based on the $dP dV$ -type process described by Eq. (25), but on a much more efficient vaporization/condensation cycle. High values of γ_{PV} are not important to the efficiency of such devices.

For at least a limited range of PVT conditions near a critical point, very high γ_{PV} have been observed and it might be interesting to look for thermoelectric materials with analogous critical points where high γ_{Ei} and ZT values might well be expected.

CONCLUSION

Several key features of thermoelectricity may be understood by analogy to the thermodynamics of an open system (referred to here as a μ - N system) which may exchange

particles and heat with its surroundings. In particular the relative magnitudes of the transport coefficients and the order of magnitude of the energy conversion efficiency largely originate in the thermodynamics of exchanging particles, at least for simple systems where scattering rates depend only weakly on energy and phonon transport can be neglected.

The analysis presented here suggests at least three distinct methods to achieve higher thermoelectric efficiency: 1) examine systems near an appropriate electronic phase transition where large γ_{Ei} (and ZT) values can be expected, in analogy to the large γ_{pV} exhibited near (for example) the gas-liquid critical conditions, 2) emphasize systems with strong interactions among the carriers where the transport matrix L may become dominated by purely transport effects (like scattering) and 3) seek to modify the 'thermoelectric cycle' to utilize more favorable thermodynamic processes.

The first two suggestions seek to improve the properties of the 'working fluid', while the final suggestion focuses attention on improving the 'engine' itself, a radically new approach to thermoelectric energy conversion.

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