

THE PHYSICAL REVIEW
AND
PHYSICAL REVIEW LETTERS

1 RESEARCH ROAD, BOX 1000
RIDGE, NEW YORK 11961-0701

Internet: pra, prb, prc, prd, pre, or prl@aps.org

Telephone: (516) 924-5533
Fax: (516) 924-5294

Telex: 971599 AMPHYSSOC
Cable: PHYSREV RIDGENY

16 October 1995

Dr. C.B. Vining
Conversion Tech
Ames Laboratory
253 Spedding
Iowa State University
Ames, IA 50011

Re: Physical basis for the present inefficiency of
thermoelectric conversion

By: C.B. Vining

BF6000

Dear Dr. Vining:

We regret the delay in obtaining a report on the above
manuscript. We are attempting to obtain one soon.

Once we have received a report, we will take appropriate
action.

Yours sincerely,

Patrick Boucher

Patrick Boucher
Senior Assistant Editor
Physical Review B

Post-It™ brand fax transmittal memo 7671		# of pages ▶	
To	Cronin Vining	From	Bruce Cook
Co.		Co.	Ames
Dept.	FYE	Phone #	
Fax #	334-887-2604	Fax #	

THE PHYSICAL REVIEW
AND
PHYSICAL REVIEW LETTERS
1 Research Road - Box 1000
Ridge, New York 11961
Fax: 516-924-5294 Phone: 516-924-5533
Internet: pr(a,b,c,d,e,or l)@aps.org

DATE 14 November 1995 FAX # 1-515 294 3709

OF PAGES INCLUDING COVER 3 (CTA)

TO: Dr. C.B. Vining AT: Iowa State University

DEPT: Conversion Tech Ames Laboratory PHONE # 15152949673

FROM: J.C. White, Asst. to the Editor

Physical Review B

MS. CODE #: BF6000

TITLE: Physical basis for the present inefficiency of thermoelectric .

AUTHORS: C.B. Vining

AMERICAN PHYSICAL SOCIETY EDITORIAL OFFICE FAX # 516-924-5294

sent reply 11/28/95
CBV

**THE PHYSICAL REVIEW
AND
PHYSICAL REVIEW LETTERS**

1 RESEARCH ROAD, BOX 1000
RIDGE, NEW YORK 11961-0701

Internet: pra, prb, prc, prd, pre, or prl@aps.org

Telephone: (516) 924-5539
Fax: (516) 924-5294

Telex: 971599 AMPHYSSOC
Cable: PHYSREV RIDGENY

14 November 1995

Dr. C.B. Vining
Conversion Tech
Ames Laboratory
253 Spedding
Iowa State University
Ames, IA 50011

Re: Physical basis for the present inefficiency of
thermoelectric conversion

By: C.B. Vining

BF6000

Dear Dr. Vining:

The above manuscript has been reviewed by one of our referees.
Comments from the report are enclosed.

These comments suggest that the present manuscript is not
suitable for publication in the Physical Review. We regret the
delay in obtaining this report.

Yours sincerely,



J. C. White
Assistant to the Editor
Physical Review B

enc.

REPORT ON BF6000

COPY

This paper addresses the efficiency of thermoelectric devices. In particular, the efficiency of thermoelectric devices depend upon the product of the temperature and the thermoelectric figure of merit, Z . The thermoelectric figure-of-merit is a property of the material: $Z = \sigma\alpha^2/\lambda$, where σ is the electrical conductivity, α is the Seebeck coefficient and λ is the thermal conductivity. For the commonly used thermoelectrics, ZT is found to have its maximum at a value close to unity.

This paper endeavors to explain why thermoelectrics based on standard semiconductors ($\text{Si}_{1-x}\text{Ge}_x$, Bi_2Te_3) have maximum values of ZT that approach 1.

1. The author first writes the electrical and thermal transport equations in terms of the standard transport coefficients, Eq. (1). From these equations the author expresses the ratio of the "thermal conductivity under the constraint of a vanishing electric field, λ_p , to the standard thermal conductivity measured with vanishing electrical current, λ_0 : $\gamma_{\text{TE}} \equiv \lambda_p/\lambda_0$, in terms of the thermoelectric figure of merit ($\gamma_{\text{TE}} = 1 + ZT$).
2. The author then considers a different problem (the equation of state for a gas) and notes that the ratio of the specific heat at constant pressure to the specific heat at constant volume, $\gamma_{\text{PV}} = C_p/C_v$, can be written in a form similar to that for γ_{TE} , Eq. (4).
3. The author then claims that the formula for the maximum efficiency of an atypical refrigeration scheme expressed in terms of γ_{PV} is analogous to that for the maximum thermoelectric conversion efficiency expressed in terms of γ_{TE} , Eqs. (7) and (9). Both efficiencies become large when their respective γ 's become large.
4. The author concludes by noting that the γ 's for the refrigeration process can become large near a critical points. Therefore, he concludes that "it may be possible to find $ZT \gg 1$ near some instability in a thermoelectric material analogous to the gas-liquid critical point." He implies that ZT will never exceed unity without such an "instability." He never describes the meaning of such an "instability" for a semiconductor in a large temperature gradient, the situation for thermoelectric energy conversion.

I think that the argument of this manuscript is unreasonable. The similarity of formulae for the maximum efficiencies for thermoelectric energy conversion to that for a refrigeration scheme is not relevant to the question of why the available thermoelectrics have $ZT < 1$.

The reason for common thermoelectrics having values of ZT that are close to unity resides in relationships between the three transport coefficients that determine Z : σ , α , and λ . In fact, we understand why the figures of merit of common thermoelectrics have the values they do. The figures of merits for common thermoelectrics are limited because of competing effects. For example, a) increasing the electrical conductivity tends to also increase the thermal conductivity and b) increasing the carrier density tends to decrease the Seebeck coefficient. These effects are well described within standard treatments of semiconductor transport.

These competing effects are not always present in more exotic systems. For example, in complicated structures the electrical and thermal transport are sometimes uncoupled from one another. For example, they can involve different portions of the structure. In addition, Seebeck coefficients can be "anomalously" large in atypical semiconductors (cage structures) in which nonstandard contributions to the Seebeck coefficient become appreciable. As a result, higher thermoelectric figures of merit than are presently available could be found from "nonstandard" materials.

The "physical basis for the present inefficiency of thermoelectric conversion" (the paper's title) does not lie in the similarity between the form of the expression for the thermoelectric efficiency with that for the efficiency of a refrigeration process. The inefficiency of present thermoelectrics is a consequence of the mechanisms that govern charge and heat transport in common semiconductors.

Submitted to
Phys. Rev. B
July 1995

A Physical Basis for the Present Inefficiency of Thermoelectric Conversion

C. B. Vining

Ames Laboratory, Iowa State University, Ames, Iowa 50011

ABSTRACT

It is shown that thermoelectric conversion is closely analogous to a kind of constant pressure-constant volume process, a process which is inherently inefficient. The observed order of magnitude of the thermoelectric figure of merit is seen to be precisely the same as the analogous properties for ideal gases, and entirely consistent with the relatively low efficiencies presently observed for thermoelectric materials. This analysis also indicates that near-Carnot efficiencies are theoretically allowed, but suggests the necessary conditions may be rather highly constrained.

PACS numbers: 84.60.-h, 72.20.Pa, 84.60.Rb, 85.80.Fi

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 significantly 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 constant pressure-constant volume conversion process which, it turns out, is inherently inefficient.

The following sections outline the essential phenomenology of thermoelectric phenomena and using a parallel formalism a certain class of pressure-volume conversion processes are described. Typical experimental results and the resulting efficiency for each system are 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 may be well approximated by

$$\begin{pmatrix} i \\ q/T \end{pmatrix} = \begin{pmatrix} \sigma_T & \sigma_T \alpha \\ \sigma_T \alpha & \lambda_E/T \end{pmatrix} \begin{pmatrix} E \\ -\nabla T \end{pmatrix} \quad (1).$$

Here i is the electric current density, E is the electric field, q is the heat current density, ∇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. (1) (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. (1), the relationships between the thermal and electrical coefficients may be succinctly summarized by

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

where ZT is the dimensionless thermoelectric figure of merit.

THERMODYNAMICS OF A PV SYSTEM

Using the ordinary thermodynamic definitions, state changes in a PV system may be represented in an entirely similar way by

$$\begin{pmatrix} dV \\ dS \end{pmatrix} = \begin{pmatrix} V\kappa_T & V\beta \\ V\beta & C_p/T \end{pmatrix} \begin{pmatrix} -dP \\ dT \end{pmatrix} \tag{3}$$

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. The symmetry Eq. (3) (i.e. that the off diagonal elements of the coefficient matrix are identical) is a result of the well known Maxwell relations.

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

$$\begin{aligned}
\gamma_{PV} &\equiv \frac{C_P}{C_V} \\
&= \frac{\kappa_T}{\kappa_S} \\
&= 1 + \frac{V\beta^2 T}{\kappa_T C_V}
\end{aligned} \tag{4},$$

where γ_{PV} has the conventional thermodynamic meaning.

TYPICAL EXPERIMENTAL RESULTS FOR THERMOELECTRICS

The thermoelectric figure of merit, ZT , has been measured for many materials and Fig. 1 shows representative results for three of the best n-type semiconductor alloys known. Even for the best known materials ZT does not 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,

$$\gamma_{PV} = 1 + \frac{2}{f} \tag{5}$$

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 $\gamma_{PV} \cong 1.67$. It is noteworthy that γ_{Ei} for many semiconductor alloys and γ_{PV} for many gases are of precisely the same order of magnitude.

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 Ref. 3) have been used to illustrate the key features in Fig. 2.

Note that $\frac{\partial P}{\partial V_T} = 0$ 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 results³ 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/cm³). The results are shown in Fig. 1 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

Define the thermoelectric efficiency as

$$\varepsilon_{Ei} \equiv \frac{-E \cdot i}{\frac{q}{T} \cdot (-\nabla T)} \quad (6)$$

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

$$\varepsilon_{Ei}^{\max} = \frac{\sqrt{\gamma_{Ei}} - 1}{\sqrt{\gamma_{Ei}} + 1} \quad (7)$$

The analogous efficiency expression for the PV system is

$$\varepsilon_{PV} \equiv \frac{dPdV}{dSdT} \quad (8)$$

Interpretation is particularly simple for the PV system. $dPdV$ 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. 2.

$dSdT$ 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. (8) 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:

$$\varepsilon_{PV}^{\max} = \frac{\sqrt{\gamma_{PV}} - 1}{\sqrt{\gamma_{PV}} + 1} \quad (9).$$

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 $dPdV$ -type process described by Eq. (9), but on a much more efficient vaporization/condensation cycle. High values of γ_{PV} are not important to the efficiency of such devices.

Since γ_{PV} is most often rather small, Eq. (9) indicates the efficiency of $dPdV$ -type energy conversion will typically be rather small. The only obvious exception is under a rather limited range of PVT conditions quite near the critical point, where high γ_{PV} and ε_{PV} are at least theoretically possible.

Therefore, the low efficiency of this type of $dPdV$ process is not the result of some sort of ‘non-ideal’ behavior of the working medium, but that the process itself is *inherently* inefficient. Whether the working gas is a Freon or an ideal gas, under most conditions γ_{PV} is on the order of 1 to 1.67 and the efficiency will be less than about 12.7% of Carnot efficiency.

CONCLUSION

In spite of the similarities of the formalism presented here, thermoelectric transport properties and thermodynamic properties are rather fundamentally different and some care must be taken when drawing conclusions based on analogy. Nevertheless, this discussion suggests, for example, that the observed order of magnitude of $ZT_{\max} \cong 1$ for a number of otherwise dissimilar thermoelectric materials is quite natural and not simply a coincidence. While there is no known simple relationship for γ_{Ei} analogous to Eq. (5) for γ_{PV} in ideal gases, each of the semiconductors represented in Fig. 2 can be considered, in some sense, nearly ideal. Each is well described by relatively simple, nearly independent electron semiconductor physics and it is perhaps ‘natural’ that their values for γ_{Ei} are of the same order of magnitude as the analogous property for ideal gases.

The similarity between the thermodynamics of infinitesimal $dPdV$ work and Ei power generation provides a plausible, physical basis for the origin of the present experimental limit of $ZT_{\max} \sim 1$ for the best known semiconductors. At the same time it can be concluded that there is no theoretical upper limit on ZT , since the completely analogous properties of real gases do in fact diverge, at least under some conditions. It may be possible, for example, to find $ZT \gg 1$ near

some instability in a thermoelectric material analogous to the gas-liquid critical point of a PV system.

ACKNOWLEDGMENTS

The author would like to thank Dr. C. Swenson for pointing out the divergence of C_p/C_v for a gas in equilibrium with its liquid. Helpful discussions with Mr. B. Cook, Mr. J. Haringa, Mr. S. Han and Mr. K. Pixius are also gratefully acknowledged.. The Ames Laboratory is operated for the U.S. Department of Energy under contract No. W-7405-ENG-82. This project was supported in part by the Radioisotope Power Support Systems Division.

REFERENCES

¹C. Wood, Rep. Prog. Phys., **51**(4), 459 (1988).

²L. Onsager, Phys. Rev. **37**, 405 (1931); **38**, 2265 (1931).

^{3,3}R. C. Downing , *Flourocarbon Refrigerants Handbook* (Prentice-Hall, Englewood Cliffs, NJ, 1988), 317-395.

FIGURE CAPTIONS

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

FIG. 2. 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.

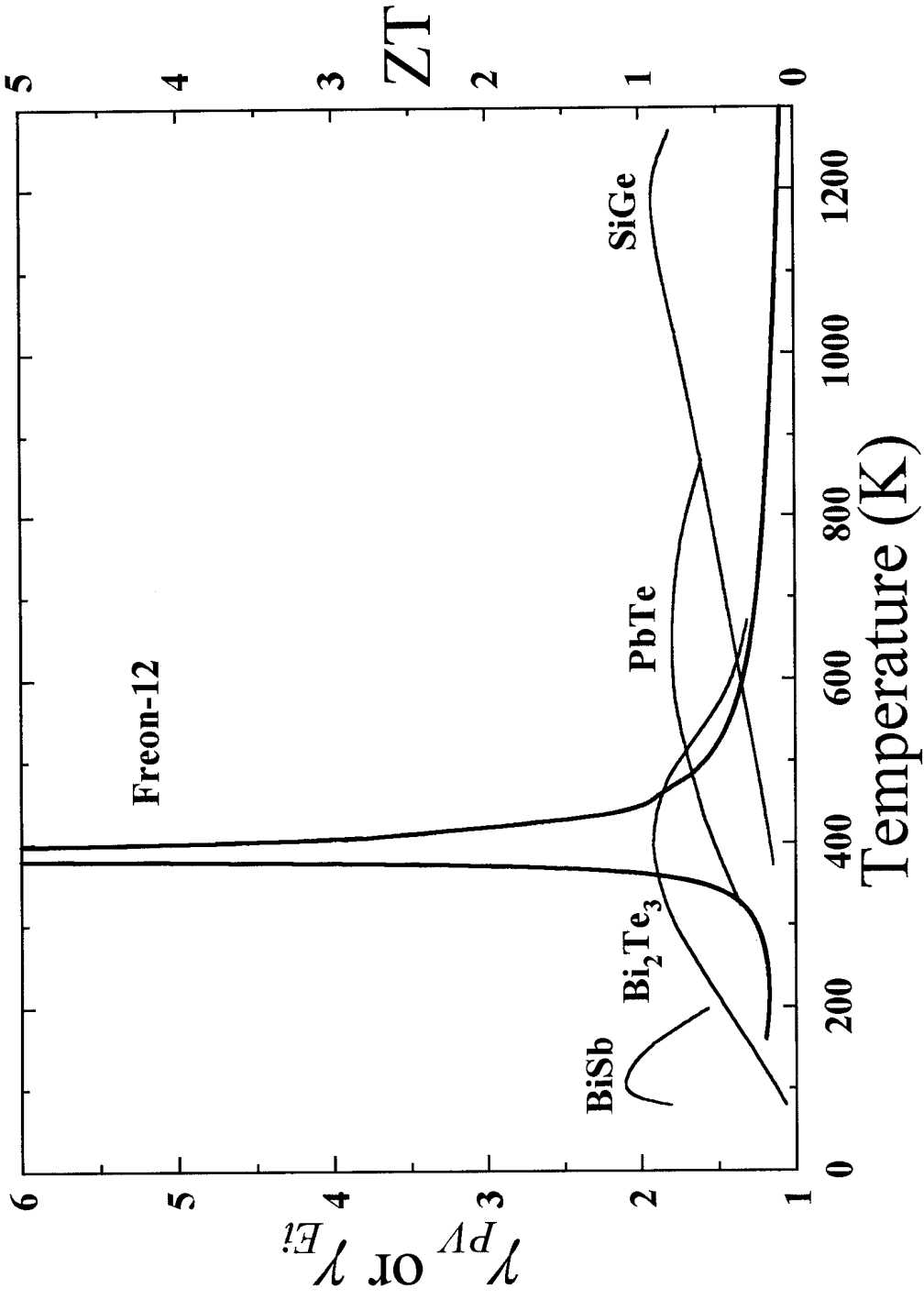


FIG. 1. Specific heat ratios, γ_{PV} for a PV system (Freon 12) and thermal conductivity ratios, $\gamma_{EI}=1+ZT$, for selected n-type semiconductor alloys as a function of temperature.

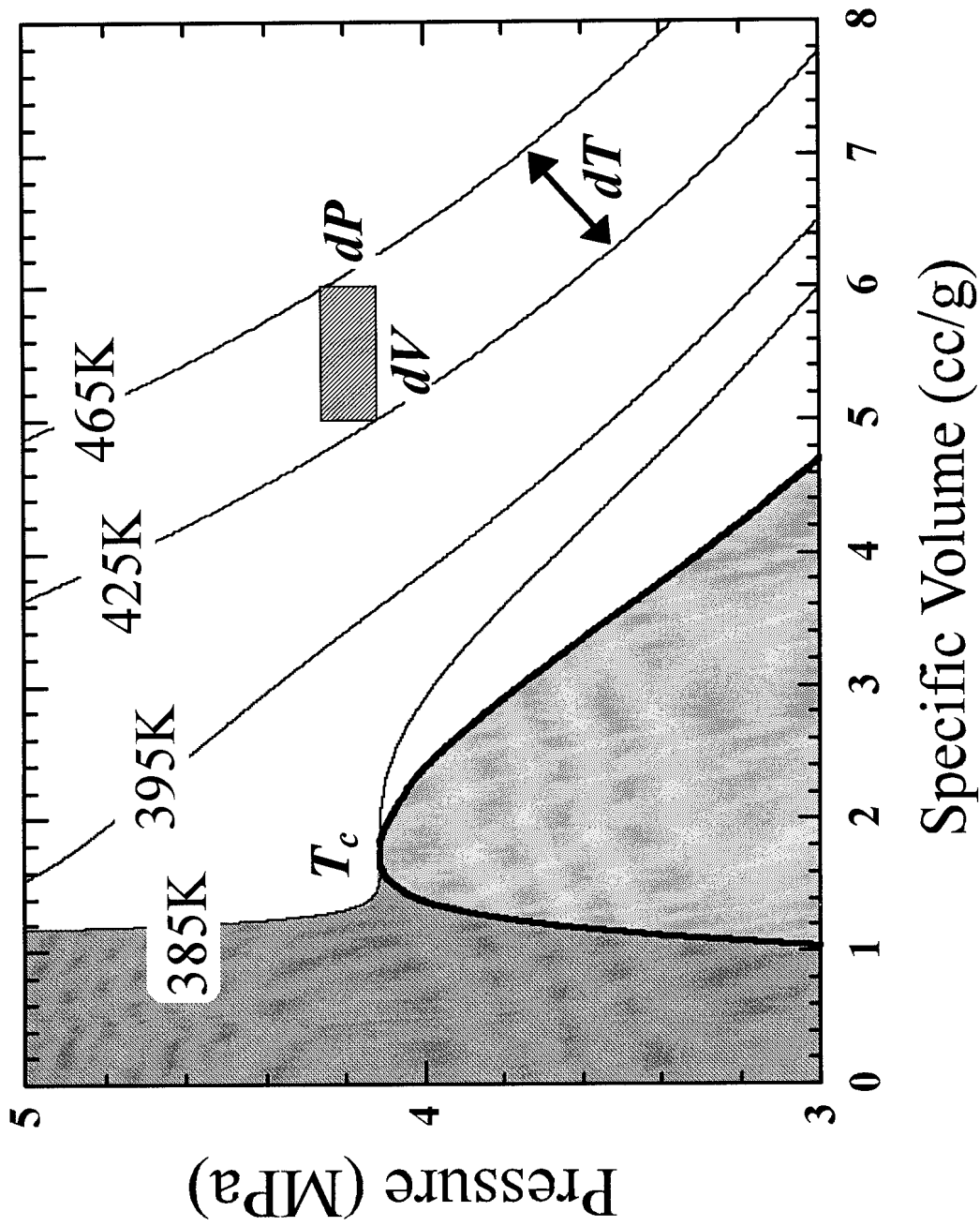


FIG. 2. PV diagram for Freon-12 (CCl_2F_2). The two phase region is light gray and the liquid is the darker gray region to the left. Isotherms are indicated by light lines and a typical $dPdV$ element is indicated by the rectangle.