

THERMOPHYSICAL PROPERTIES OF MATTER
VOLUME 5

SPECIFIC HEAT

Nonmetallic Solids

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SPECIFIC HEAT

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THERMOPHYSICAL PROPERTIES OF MATTER
The TPRC Data Series

A Comprehensive Compilation of Data by the
Thermophysical Properties Research Center (TPRC), Purdue University

Y. S. Touloukian, Series Editor
C. Y. Ho, Series Technical Editor

- Volume 1. Thermal Conductivity–Metallic Elements and Alloys
- Volume 2. Thermal Conductivity–Nonmetallic Solids
- Volume 3. Thermal Conductivity–Nonmetallic Liquids and Gases
- Volume 4. Specific Heat–Metallic Elements and Alloys
- Volume 5. Specific Heat–Nonmetallic Solids
- Volume 6. Specific Heat–Nonmetallic Liquids and Gases
- Volume 7. Thermal Radiative Properties–Metallic Elements and Alloys
- Volume 8. Thermal Radiative Properties–Nonmetallic Solids
- Volume 9. Thermal Radiative Properties–Coatings
- Volume 10. Thermal Diffusivity
- Volume 11. Viscosity
- Volume 12. Thermal Expansion–Metallic Elements and Alloys
- Volume 13. Thermal Expansion–Nonmetallic Solids

New data on thermophysical properties are being constantly accumulated at TPRC. Contact TPRC and use its interim updating services for the most current information.

“In this work, when it shall be found that much is omitted, let it not be forgotten that much likewise is performed...”

SAMUEL JOHNSON, A.M.

From last paragraph of Preface to his two-volume *Dictionary of the English Language*, Vol. I, page 5, 1755, London, Printed by Strahan.

Foreword

In 1957, the Thermophysical Properties Research Center (TPRC) of Purdue University, under the leadership of its founder, Professor Y. S. Touloukian, began to develop a coordinated experimental, theoretical, and literature review program covering a set of properties of great importance to science and technology. Over the years, this program has grown steadily, producing bibliographies, data compilations and recommendations, experimental measurements, and other output. The series of volumes for which these remarks constitute a foreword is one of these many important products. These volumes are a monumental accomplishment in themselves, requiring for their production the combined knowledge and skills of dozens of dedicated specialists. The Thermophysical Properties Research Center deserves the gratitude of every scientist and engineer who uses these compiled data.

The individual nontechnical citizen of the United States has a stake in this work also, for much of the science and technology that contributes to his well-being relies on the use of these data. Indeed, recognition of this importance is indicated by a mere reading of the list of the financial sponsors of the Thermophysical Properties Research Center; leaders of the technical industry of the United States and agencies of the Federal Government are well represented.

Experimental measurements made in a laboratory have many potential applications. They might be used, for example, to check a theory, or to help design a chemical manufacturing plant, or to compute the characteristics of a heat exchanger in a nuclear power plant. The progress of science and technology demands that results be published in the open literature so that others may use them. Fortunately for progress, the useful data in any single field are not scattered throughout the tens of thousands of technical journals published throughout the world. In most fields, fifty percent of the useful work appears in no more than thirty or forty journals. However, in the case of TPRC, its field is so broad

that about 100 journals are required to yield fifty percent. But that other fifty percent! It is scattered through more than 3500 journals and other documents, often items not readily identifiable or obtainable. Nearly 50,000 references are now in the files.

Thus, the man who wants to use existing data, rather than make new measurements himself, faces a long and costly task if he wants to assure himself that he has found all the relevant results. More often than not, a search for data stops after one or two results are found—or after the searcher decides he has spent enough time looking. Now with the appearance of these volumes, the scientist or engineer who needs these kinds of data can consider himself very fortunate. He has a single source to turn to; thousands of hours of search time will be saved, innumerable repetitions of measurements will be avoided, and several billions of dollars of investment in research work will have been preserved.

However, the task is not ended with the generation of these volumes. A critical evaluation of much of the data is still needed. Why are discrepant results obtained by different experimentalists? What undetected sources of systematic error may affect some or even all measurements? What value can be derived as a "recommended" figure from the various conflicting values that may be reported? These questions are difficult to answer, requiring the most sophisticated judgment of a specialist in the field. While a number of the volumes in this series do contain critically evaluated and recommended data, these are still in the minority. The data are now being more intensively evaluated by the staff of TPRC as an integral part of the effort of the National Standard Reference Data System (NSRDS). The task of the National Standard Reference Data System is to organize and operate a comprehensive program to prepare compilations of critically evaluated data on the properties of substances. The NSRDS is administered by the National Bureau of Standards under a directive from the Federal Council for Science

and Technology, augmented by special legislation of the Congress of the United States. TPRC is one of the national resources participating in the National Standard Reference Data System in a united effort to satisfy the needs of the technical community for readily accessible, critically evaluated data.

As a representative of the NBS Office of Standard Reference Data, I want to congratulate Professor Touloukian and his colleagues on the accomplishments represented by this Series of reference data

books. Scientists and engineers the world over are indebted to them. The task ahead is still an awesome one and I urge the nation's private industries and all concerned Federal agencies to participate in fulfilling this national need of assuring the availability of standard numerical reference data for science and technology.

EDWARD L. BRADY

*Associate Director for Information Programs
National Bureau of Standards*

Preface

Thermophysical Properties of Matter, the TPRC Data Series, is the culmination of twelve years of pioneering effort in the generation of tables of numerical data for science and technology. It constitutes the restructuring, accompanied by extensive revision and expansion of coverage, of the original *TPRC Data Book*, first released in 1960 in loose-leaf format, 11"×17" in size, and issued in June and December annually in the form of supplements. The original loose-leaf *Data Book* was organized in three volumes: (1) metallic elements and alloys, (2) nonmetallic elements, compounds, and mixtures which are solid at N.T.P., and (3) nonmetallic elements, compounds, and mixtures which are liquid or gaseous at N.T.P. Within each volume, each property constituted a chapter.

Because of the vast proportions the *Data Book* began to assume over the years of its growth and the greatly increased effort necessary in its maintenance by the user, it was decided in 1967 to change from the loose-leaf format to a conventional publication. Thus, the December 1966 supplement of the original *Data Book* was the last supplement disseminated by TPRC.

While the manifold physical, logistic, and economic advantages of the bound volume over the loose-leaf oversize format are obvious and welcome to all who have used the unwieldy original volumes, the assumption that this work will no longer be kept on a current basis because of its bound format would not be correct. Fully recognizing the need of many important research and development programs which require the latest available information, TPRC has instituted a *Data Update Plan* enabling the subscriber to inquire, by telephone if necessary, for specific information and receive, in many instances, same-day response on any new data processed or revision of published data since the latest edition. In this context, the TPRC Data Series departs drastically from the conventional handbook and giant multivolume classical works, which are no longer adequate media for the dissemination of

numerical data of science and technology without a continuing activity on contemporary coverage. The loose-leaf arrangements of many works fully recognize this fact and attempt to develop a combination of bound volumes and loose-leaf supplement arrangements as the work becomes increasingly large. TPRC's *Data Update Plan* is indeed unique in this sense since it maintains the contents of the TPRC Data Series current and live on a day-to-day basis between editions. In this spirit, I strongly urge all purchasers of these volumes to complete in detail and return the *Volume Registration Certificate* which accompanies each volume in order to assure themselves of the continuous receipt of annual listing of corrigenda during the life of the edition.

The TPRC Data Series consists initially of 13 independent volumes. The initial ten volumes will be published in 1970, and the remaining three by 1972. It is also contemplated that subsequent to the first edition, each volume will be revised, updated, and reissued in a new edition approximately every fifth year. The organization of the TPRC Data Series makes each volume a self-contained entity available individually without the need to purchase the entire Series.

The coverage of the specific thermophysical properties represented by this Series constitutes the most comprehensive and authoritative collection of numerical data of its kind for science and technology.

Whenever possible, a uniform format has been used in all volumes, except when variations in presentation were necessitated by the nature of the property or the physical state concerned. In spite of the wealth of data reported in these volumes, it should be recognized that all volumes are not of the same degree of completeness. However, as additional data are processed at TPRC on a continuing basis, subsequent editions will become increasingly more complete and up to date. Each volume in the Series basically comprises three sections, consisting of a text, the body of numerical data with source references, and a material index.

The aim of the textual material is to provide a complementary or supporting role to the body of numerical data rather than to present a treatise on the subject of the property. The user will find a basic theoretical treatment, a comprehensive presentation of selected works which constitute reviews, or compendia of empirical relations useful in estimation of the property when there exists a paucity of data or when data are completely lacking. Established major experimental techniques are also briefly reviewed.

The body of data is the core of each volume and is presented in both graphical and tabular format for convenience of the user. Every single point of numerical data is fully referenced as to its original source and no secondary sources of information are used in data extraction. In general, it has not been possible to critically scrutinize all the original data presented in these volumes, except to eliminate perpetuation of gross errors. However, in a significant number of cases, such as for the properties of liquids and gases and the thermal conductivity of all the elements, the task of full evaluation, synthesis, and correlation has been completed. It is hoped that in subsequent editions of this continuing work, not only new information will be reported but the critical evaluation will be extended to increasingly broader classes of materials and properties.

The third and final major section of each volume is the material index. This is the key to the volume, enabling the user to exercise full freedom of access to its contents by any choice of substance name or detailed alloy and mixture composition, trade name, synonym, etc. Of particular interest here is the fact that in the case of those properties which are reported in separate companion volumes, the material index in each of the volumes also reports the contents of the other companion volumes.* The sets of companion volumes are as follows:

Thermal conductivity:	Volumes 1, 2, 3
Specific heat:	Volumes 4, 5, 6
Radiative properties:	Volumes 7, 8, 9
Thermal expansion:	Volumes 12, 13

The ultimate aims and functions of TPRC's Data Tables Division are to extract, evaluate, reconcile, correlate, and synthesize all available data for the thermophysical properties of materials with

the result of obtaining internally consistent sets of property values, termed the "recommended reference values." In such work, gaps in the data often occur, for ranges of temperature, composition, etc. Whenever feasible, various techniques are used to fill in such missing information, ranging from empirical procedures to detailed theoretical calculations. Such studies are resulting in valuable new estimation methods being developed which have made it possible to estimate values for substances and/or physical conditions presently unmeasured or not amenable to laboratory investigation. Depending on the available information for a particular property and substance, the end product may vary from simple tabulations of isolated values to detailed tabulations with generating equations, plots showing the concordance of the different values, and, in some cases, over a range of parameters presently unexplored in the laboratory.

The TPRC Data Series constitutes a permanent and valuable contribution to science and technology. These constantly growing volumes are invaluable sources of data to engineers and scientists, sources in which a wealth of information heretofore unknown or not readily available has been made accessible. We look forward to continued improvement of both format and contents so that TPRC may serve the scientific and technological community with ever-increasing excellence in the years to come. In this connection, the staff of TPRC is most anxious to receive comments, suggestions, and criticisms from all users of these volumes. An increasing number of colleagues are making available at the earliest possible moment reprints of their papers and reports as well as pertinent information on the more obscure publications. I wish to renew my earnest request that this procedure become a universal practice since it will prove to be most helpful in making TPRC's continuing effort more complete and up to date.

It is indeed a pleasure to acknowledge with gratitude the multisource financial assistance received from over fifty of TPRC's sponsors which has made the continued generation of these tables possible. In particular, I wish to single out the sustained major support being received from the Air Force Materials Laboratory-Air Force Systems Command, the Office of Standard Reference Data-National Bureau of Standards, and the Office of Advanced Research and Technology-National Aeronautics and Space Administration. TPRC is indeed proud to have been designated as a National Information Analysis Center for the Department of Defense as well as a component of the National

*For the first edition of the Series, this arrangement was not feasible for Volume 7 due to the sequence and the schedule of its publication. This situation will be resolved in subsequent editions.

Standard Reference Data System under the cognizance of the National Bureau of Standards.

While the preparation and continued maintenance of this work is the responsibility of TPRC's Data Tables Division, it would not have been possible without the direct input of TPRC's Scientific Documentation Division and, to a lesser degree, the Theoretical and Experimental Research Divisions. The authors of the various volumes are the senior staff members in responsible charge of the work. It should be clearly understood, however, that many have contributed over the years and their contributions are specifically acknowledged in each volume. I wish to take this opportunity to personally

thank those members of the staff, research assistants, graduate research assistants, and supporting graphics and technical typing personnel without whose diligent and painstaking efforts this work could not have materialized.

Y. S. TOULOUKIAN

*Director
Thermophysical Properties Research Center
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Purdue University
Lafayette, Indiana
July 1969

Introduction to Volume 5

This volume of *Thermophysical Properties of Matter*, the TPRC Data Series, was initiated in recent years and follows the general format of the Center's work on thermal conductivity.

The volume comprises three major sections: the front text material together with its bibliography, the main body of numerical data and its references, and the material index.

The text material is intended to assume a role complementary to the main body of numerical data, the presentation of which is the primary purpose of this volume. It is felt that a concise discussion of the theoretical nature of the property under consideration together with a review of predictive procedures and recognized experimental techniques will be appropriate in a major reference work of this kind. The extensive reference citations given in the text should lead the interested reader to a highly comprehensive literature for a detailed study. It is hoped, however, that enough detail is presented for this volume to be self-contained for the practical user.

The main body of the volume consists of the presentation of numerical data compiled over the years in a most comprehensive and meticulous manner. The scope of coverage includes most non-metallic materials of engineering importance which are in the solid state at normal temperature and pressure. The extraction of all data directly from their original sources ensures freedom from errors of transcription. Furthermore, some gross errors appearing in the original source documents have been corrected. The organization and presentation of the data together with other pertinent information in the use of the tables and figures are discussed in detail in the text of the section entitled *Numerical Data*.

It is regrettable that the authors have not yet had the time to review and evaluate critically the extensive data compiled in this volume. However, it is hoped that the user will be able to exercise proper selectivity and discretion among conflicting sets of data based on the extensive information reported for each set in the accompanying specification tables.

As stated earlier, all data have been obtained from their original sources and each data set is so referenced. TPRC has in its files all documents cited in this volume. Those that cannot be readily obtained elsewhere are available from TPRC in microfiche form.

The material index at the end of this volume covers the contents of all three companion volumes (Volumes 4, 5, and 6) on specific heat. It is hoped that the user will find these comprehensive indices helpful.

This work has grown out of activities made possible principally through the support of the Air Force Materials Laboratory—Air Force Systems Command, under the monitorship of Mr. John H. Charlesworth. In the preparation of this volume we have drawn most heavily upon the scientific literature and hence we feel a debt of gratitude to the authors of the referenced articles.

While this volume is primarily intended as a reference work for the designer, researcher, experimentalist, and theoretician, the teacher at the graduate level may also use it as a teaching tool to point out to his students the topography of the state of knowledge on the specific heat of nonmetals. We believe there is also much food for reflection by the specialist and the academician concerning the meaning of "original" investigation and its "information content."

The authors are keenly aware of the possibility of many weaknesses in a work of this scope. We hope that we will not be judged too harshly and that we will receive suggestions regarding references omitted, additional material groups needing more detailed treatment, improvements in presentation, and, most important, any inadvertent errors. If the *Volume 2 Registration Certificate* accompanying this volume is returned, the reader will assure himself of receiving annually a list of corrigenda as possible errors come to our attention.

Lafayette, Indiana
July 1969

Y. S. TOULOUKIAN
E. H. BUYCO

Theory, Estimation, and Measurement

Notation

A	Grüneisen constant; Cross-sectional area	Q	Amount of heat absorbed or removed from the system
a	Lattice constant; Empirical constant	R	Gas constant, $8.3143 \text{ J K}^{-1} \text{ g-mol}^{-1}$
b	Empirical constant	s	Spin vector
c, C	Heat capacity of mass m , specific heat per unit mass	T	Temperature, K
C_a, C_f	Constant which depends on particular type of lattice and on crystal structure, respectively	t	Time
C_e	Electronic specific heat	V	Volume
C_p, C_v	Specific heat at constant pressure and constant volume, respectively	v	Specific volume
d	Density	W	Work done on or by the system
e	Base of natural logarithm, 2.71828	x, x_m	$h\nu/kT$ and $h\nu_D/kT$, respectively, as used in equation (17)
E	Total energy of an oscillator, particle, or system; Internal energy; Voltage	X_i	Atomic mole or mass fraction of i th component in an alloy or mixture
H	Enthalpy	α, α_f	Coefficient of thermal linear expansion, and a constant which depends on crystal structure, respectively
$(\Delta H)_f$	Heat of fusion	β	Coefficient of isobaric volumetric expansion; Constant in Debye cube law
h	Planck constant, $6.6262 \times 10^{-27} \text{ erg sec}$	γ	Constant in the electronic specific heat relation (26)
I	Electrical current	θ_D, θ_E	Characteristic Debye temperature and Einstein temperature, $h\nu_D/k$ and $h\nu/k$, respectively
J, J'	Quantum mechanical exchange constants	ν	Frequency of oscillation of a particle
K	Calibration factor in ice drop calorimeter	ν_D	Debye frequency
k	Boltzmann constant, $1.3806 \times 10^{-16} \text{ erg K}^{-1}$	ω	Natural angular frequency
L	Linear dimension	ρ	Electrical resistivity
m	Mass of a particle, system, or specimen	ρ_e	Number of free electrons per unit volume
m_e	Mass of an electron	ϵ	Energy of an oscillation
n	Integer, 0, 1, 2, 3, . . .	π	Mathematical constant, 3.14159 . . .
N_A	Avogadro's number, $6.0222 \times 10^{23} \text{ g-mol}^{-1}$	κ_T	Isothermal compressibility, as used in equation (36)
N_e	Number of electrons per gram atom		
p	Momentum of a particle; Pressure of a gas		
q	Direction coordinate from equilibrium position		

Theory of Specific Heat of Solids

1. INTRODUCTION

Rapid advances in the frontiers of science and technology have brought about a general realization of the fact that the present limitations in many technical developments are a direct result of inadequate knowledge of the thermophysical properties of materials. In the high-temperature range ($T > 1000$ K), interest in the determination of specific heats of materials has been hastened because of the requirements in space programs as well as industrial applications. The need for data at high temperatures has advanced our knowledge in many areas of solid state studies such as lattice vibrations, energy levels in magnetic solids, electronic distributions, and many other atomic and molecular phenomena.

The measurement of specific heat at cryogenic temperatures ($C_p \cong C_v$ for $T \leq 4$ K) provides us with a direct means to test theoretical models of a system. For instance, precise specific heat measurements were needed to test the validity of Debye's and Einstein's theory for specific heat of solids at low temperatures. Finally, knowledge of accurate specific heat data at low temperature is very useful in studies of cryogenic techniques.

2. DEFINITIONS

When a quantity of heat Q is added to a system so that there is a change in temperature, $T_2 - T_1$, then the mean heat capacity of the mass m of the substance is defined by

$$\bar{c} = \frac{Q}{T_2 - T_1} \quad (1)$$

The limiting value of the above ratio as the temperature changes by dT is defined as the true heat capacity, i.e.,

$$c = \frac{dQ^*}{dT} \quad (2)$$

* dQ is used instead of dQ to indicate that it is not an exact differential.

In order to obtain a quantity that is independent of the mass, m , of a substance, equation (2) is divided by m ; i.e.,

$$C = \frac{c}{m} = \frac{dQ}{m dT} \quad (3)$$

The quantity q represents the amount of heat per unit mass, so that equation (3) may also be written as

$$C = \frac{dq}{dT} \quad (4)$$

Raising the temperature of a unit mass of a substance by an amount dT , however, does not define the process in a thermodynamic sense; for instance, it will take a different amount of heat dq if the process is at constant pressure than when the process is at constant volume. As a matter of fact there are an infinite number of different processes for a system at temperature T to change to a temperature $T + dT$. It is clear, therefore, that an infinite number of specific heats could also be defined for a substance. The two processes that are most commonly used in thermodynamics are those at constant volume and constant pressure. For these two processes equation (4) may be written

$$C_p = \left(\frac{dq}{dT} \right)_p \quad (5)$$

and

$$C_v = \left(\frac{dq}{dT} \right)_v \quad (6)$$

Experimentally, the values of the specific heat measured are either at constant pressure, C_p , or at constant volume, C_v . The units most commonly used for specific heat are $\text{cal g}^{-1} \text{K}^{-1}$, $\text{Btu lb}^{-1} \text{F}^{-1}$, joules $\text{kg}^{-1} \text{K}^{-1}$. The units for molar or atomic specific heat are $\text{cal g-mol}^{-1} \text{K}^{-1}$, $\text{Btu lb-mol}^{-1} \text{F}^{-1}$, joules $\text{kg-mol}^{-1} \text{K}^{-1}$, $\text{cal g-atom}^{-1} \text{K}^{-1}$, joules $\text{kg-atom}^{-1} \text{K}^{-1}$, etc.

3. DULONG AND PETIT'S LAW

In 1819 Dulong and Petit [9] published the results of their measurements on the specific heat at constant pressure of thirteen solid elements at room temperature. From these measurements, they observed that the product of the specific heat at constant pressure and the atomic weight was approximately a constant, about $6 \text{ cal g-atom}^{-1} \text{ K}^{-1}$. Subsequent researches, extending from 1840 to 1862, revealed the general applicability of the Dulong and Petit's law to several metallic elements, when the specific heat at constant pressure was determined at temperatures sufficiently below their melting point but not far below room temperature. During the same period an important extension of Dulong and Petit's law was applied to chemical compounds, i.e., the molar specific heat of a compound is equal to the sum of the atomic specific heats of its constituent elements. This law which is generally referred to as the Kopp-Neumann law [32] has also been applied to predict the atomic specific heat of alloys. For alloys, the atomic specific heat is equal to the sum of the product of the atomic specific heat of each constituent element and its atomic fraction. If an alloy consists of elements 1, 2, 3, ..., n , with atomic fraction $X_1, X_2, X_3, \dots, X_n$ and atomic specific heat $C_{p1}, C_{p2}, C_{p3}, \dots, C_{pn}$, then the atomic specific heat of the alloy is

$$C_p = \sum_{i=1}^n X_i C_{pi} \quad (7)$$

Equation (7) should be applied with caution for alloys especially near magnetic and phase transitions. Bottema and Jaeger [5] have applied the Kopp-Neumann law to the alloy Ag_3Au and they found that the experimental data on the specific heat at constant pressure of this alloy agree closely with the calculated values between 0 C to 400 C. Between 400 C and 800 C, the values obtained from the Kopp-Neumann law were 0.5 percent to 1.8 percent higher than the experimental results. Buyco [46] calculated the specific heat of the alloys of aluminum, beryllium, nickel, and iron between 300 K to 1000 K and found the calculated values agree with the experimental data to within 5 percent.

The theoretical justification of the law of Dulong and Petit was demonstrated by Boltzmann in 1871. The results obtained previously by Dulong and Petit also follow from Boltzmann's equipartition of energy theorem. Complete and detailed derivation of this theorem is discussed elsewhere [15, 20, 21, 33, and 43].

The following is a brief exposition. The energy of a linear harmonic oscillator consists of kinetic and potential energies, i.e.,

$$E = \frac{p^2}{2m} + \frac{m\omega^2 q^2}{2} \quad (8)$$

where p is the momentum, m is the mass, ω is the natural angular frequency, q is the distance from equilibrium position, and E is the total energy of an oscillator. From the theorem of equipartition of energy [15, 20, 21, 31], each degree of freedom contributes $(kT/2)$ to the energy of a particle in equilibrium. A three-dimensional oscillator which has six degrees of freedom will therefore have an internal energy of $3kT$ at thermal equilibrium. A gram-atom of an element has N_A atoms; hence, the internal energy is $3N_A kT$. The specific heat at constant volume is obtained by differentiating the internal energy with respect to temperature at constant volume, i.e.,

$$\left(\frac{\partial E}{\partial T}\right)_v = C_v = 3N_A k \quad (9)$$

where N_A is the Avogadro constant and k is the Boltzmann constant. The product of Avogadro constant and Boltzmann constant is equal to the gas constant R . Therefore:

$$C_v = 3R \cong 5.96 \text{ cal mol}^{-1} \text{ K}^{-1}$$

Hence, the Dulong and Petit value of about $6 \text{ cal mol}^{-1} \text{ deg}^{-1}$ for the specific heat of metallic solids can be accounted for on the basis of classical statistical mechanics. However, the observation of Dulong and Petit was short lived. In 1875 Weber [48] showed that the atomic specific heat of silicon, boron, and carbon are considerably lower than the values predicted by Dulong and Petit. For example, the atomic specific heat of crystalline silicon, boron, and diamond were found to be 4.8, 2.7, and 1.8 $\text{cal mol}^{-1} \text{ deg}^{-1}$, respectively, at room temperature. Subsequent specific heat measurements at low temperatures ($T < 300 \text{ K}$) revealed that the specific heat of solids increased rapidly with temperature and almost leveled off about their Debye temperature. Classical theory does not explain this behavior for solids. It should also be noted that classical theory encounters the same difficulty in the behavior of molar specific heats.

4. EINSTEIN'S SPECIFIC HEAT THEORY

Einstein [10] proposed a simple model to account

for the decrease in the specific heat at low temperatures below the value $3R$ per mole which was obtained at elevated temperatures. His oversimplified physical model considers the thermal properties of the vibrations of a lattice of N_A atoms as a set of $3N_A$ independent harmonic oscillators in one dimension, each with the same frequency, ν . He then quantized the energy of the oscillators in accordance with the results obtained by Planck. According to Planck, a harmonic oscillator does not have a continuous energy spectrum but can accept energy values equal to an integer times $h\nu$, where ν is the frequency of oscillations and h is the Planck constant. Hence the possible energy levels of an oscillator may be given by

$$\epsilon = n h \nu \quad n = 0, 1, 2, 3, \dots$$

The average energy of an oscillator at temperature T , according to the well known Planck formula [7, 20, 21, 32], is

$$\bar{\epsilon} = \frac{h\nu}{\exp(h\nu/kT) - 1} \quad (10)$$

In Einstein's model the vibrational energy of a solid element containing N_A atoms is $3N_A$ times the average energy of an oscillator, i.e.,

$$\bar{E} = 3N_A \frac{h\nu}{\exp(h\nu/kT) - 1} \quad (11)$$

The results obtained from quantum mechanics however showed that the average energy of an oscillator [7, 15] should be written as

$$\bar{\epsilon} = \frac{h\nu}{2} + \frac{h\nu}{\exp(h\nu/kT) - 1} \quad (12)$$

instead of as in equation (10).

The result obtained for the specific heat by differentiating equation (10) is the same as that obtained from equation (12). In any case the specific heat for one atom of an element is

$$\left(\frac{\partial E}{\partial T}\right)_v = C_v = \frac{3N_A k (h\nu/kT)^2 \exp(h\nu/kT)}{[\exp(h\nu/kT) - 1]^2} \quad (13)$$

For convenience, the characteristic Einstein temperature defined by $\theta_E = h\nu/k$ may be introduced in equation (13) to obtain

$$C_v = \frac{3R(\theta_E/T)^2 \exp(\theta_E/T)}{[\exp(\theta_E/T) - 1]^2} \quad (14)$$

In the high-temperature range with $T \gg \theta_E$ [15, 20, 21, 32], equation (14) upon expansion in power series becomes

$$C_v \cong 3R \left[1 - \frac{1}{12} \left(\frac{\theta_E}{T} \right)^2 \right] \quad (15)$$

When the value of $[(\theta_E/T)^2/12]$ is such that it is very much smaller than 1, then Einstein's theory yields the classical Dulong and Petit value of $6 \text{ cal mol}^{-1} \text{ deg}^{-1}$.

In the low-temperature region $T \ll \theta_E$, equation (14) may be written approximately as

$$C_v \cong 3R \left(\frac{\theta_E}{T} \right)^2 \exp(-\theta_E/T) \quad (16)$$

According to equation (16), the low-temperature specific heat of solids should approach zero exponentially. Experimental evidence indicates that C_v approaches zero more slowly than this. The reason for the discrepancy between Einstein's theoretical prediction and the experimental results may be explained on the basis of the assumption made in the theory that each atom in a solid vibrates independently of the others but with precisely the same frequency. However, in spite of the weakness in Einstein's theory, his pioneering work opened the way for the application of quantum theory to the specific heat of solids.

5. DEBYE'S SPECIFIC HEAT THEORY

From the point of view of the wave whose wavelength is large compared with the interatomic distances, a crystal may appear like a continuum. The fundamental assumption of Debye [6] is that the continuum model may be employed for all possible vibrational modes of the crystal. Debye has given a limit to the total number of vibrational modes equal to $3N_A$, where N_A is the number of atoms in a gram atom of an element. In this case, the frequency spectrum which corresponds to an ideal continuum is cut off in order to comply with a total of $3N_A$ modes. This procedure should provide a maximum frequency ν_D (Debye frequency) which is common to both the longitudinal and transverse modes. By associating with each vibrational mode a harmonic oscillator of the same frequency, Debye obtained the following expression [7, 15, 20, 21, 32] for the vibrational energy:

$$\bar{E} = 9N_A h \nu_D \left(\frac{kT}{h\nu_D} \right)^4 \int_0^{x_m} \frac{x^3 dx}{e^x - 1} \quad (17)$$

where

$$x = h\nu/kT \quad x_m = h\nu_D/kT$$

Clearly, when $T \gg \theta_D$, x_m is small compared with unity for the whole integration range. In this case $e^x - 1 \cong x$ so that equation (17) could easily be integrated to obtain the expression

$$\bar{E} \cong 3N_A kT \quad (18)$$

Then

$$\left(\frac{\partial \bar{E}}{\partial T}\right)_v = C_v = 3N_A k = 3R \cong 6 \text{ cal mol}^{-1} \text{ deg}^{-1}$$

a result agreeing with classical theory.

At very low temperatures, $T \ll \theta_D$, the upper limit of integration in equation (17) may be replaced by infinity since $h\nu/kT \rightarrow \infty$ as $T \rightarrow 0$. It is now possible to integrate equation (17) as follows [51]

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = 6 \sum_{n=1}^\infty \frac{1}{n^4} = \frac{\pi^4}{15} \quad (19)$$

Hence

$$\bar{E} = \frac{3}{5} \pi^4 N_A k T \left(\frac{T}{\theta_D}\right)^3 \quad (20)$$

and

$$C_v = \left(\frac{\partial \bar{E}}{\partial T}\right)_v = \frac{12}{5} \pi^4 N_A k \left(\frac{T}{\theta_D}\right)^3 \quad (21)$$

or

$$C_v = \frac{12}{5} \pi^4 R \left(\frac{T}{\theta_D}\right)^3 \quad (22)$$

For one atom or one mole of a substance, $R = 1.987 \text{ cal mol}^{-1} \text{ deg}^{-1}$ so that equation (22) may be written as

$$C_v = 464.5 \left(\frac{T}{\theta_D}\right)^3 \text{ cal mol}^{-1} \text{ deg}^{-1} \quad T < \left(\frac{\theta_D}{50}\right) \quad (23)$$

Debye's theory predicts a cube law dependence of the specific heat of the elements for temperatures $T < (\theta_D/10)$. The range of validity of this law [15] has now been restricted to $T < (\theta_D/50)$ as a result of more recent theoretical work on specific heat studies. The predictions of Debye's theory agree quite well with experimental values of the specific heat of solids and is a definite improvement over Einstein's work.

Due to improved calorimetric measurements at low temperatures ($T < 5 \text{ K}$), in recent years accurate

specific heat values revealed that Debye's equation for C_v does not fit the experimental results precisely. Furthermore, it was observed that θ_D , which according to Debye's theory is a constant, did in fact vary with temperature. The deficiency of the Debye theory may be explained on the basis of the approximation made in treating solids as a continuous elastic media and neglecting the discreteness of the atoms.

Further improvements on Debye's theory was developed by Born and Karman [4]. They calculated the frequency spectrum by considering the lattice modes of vibration for a particular crystal structure under investigation. The method is involved so that one is referred to the original work [4] for detailed discussion.

6. ELECTRONIC SPECIFIC HEAT

In 1900, Drude [8] suggested a model for a free-electron theory of metals. He assumed that metals contain free electrons in thermal equilibrium with the atoms of the solid. He further assumed that the potential energy of the free electrons is equal to the product of the number of electrons per unit volume and the average energy of an electron. The essential feature in the problem is the determination of the number of electrons with energy between E and $E + dE$. Classical theory using Maxwell-Boltzmann statistics [2, 8, 15, 20, 21, 32, 43], would give an expression for the electronic specific heat as

$$C_e = \frac{3}{2} N_e k \quad (24)$$

Using Fermi-Dirac statistics [7, 15, 19, 20, 21, 31, 32], the following expression for the electronic specific heat may be obtained at low temperatures:

$$C_e = \pi^2 R (2m_e k/h^2) \left(\frac{\pi}{3\rho_e}\right)^{2/3} T \quad (25)$$

or simply

$$C_e = \gamma T \quad (26)$$

where ρ_e is the number of free electrons per unit volume, γ is the proportionality constant, T is the absolute temperature, N_e is the number of electrons per gram atom, m_e is the mass of an electron, k is the Boltzmann constant, h is the Planck constant, R is the gas constant, and C_e is the electronic specific heat.

The specific heat of metals below the Debye temperature and "very much" below the Fermi temperature [15, 19, 20, 21, 32] may be expressed as