## 19.1 INTRODUCTION

*Thermal property* refers to the response of a material to the application of heat. As a solid absorbs energy in the form of heat, its temperature rises and its dimensions increase. The energy may be transported to cooler regions of the specimen if temperature gradients exist, and ultimately, the specimen may melt. Heat capacity, thermal expansion, and thermal conductivity are properties that are often critical in the practical utilization of solids.

## 19.2 HEAT CAPACITY

**heat capacity**

A solid material, when heated, experiences an increase in temperature signifying that some energy has been absorbed. **Heat capacity** is a property that is indicative of a material's ability to absorb heat from the external surroundings; it represents the amount of energy required to produce a unit temperature rise. In mathematical terms, the heat capacity $C$ is expressed as follows:

Definition of heat capacity—ratio of energy change (energy gained or lost) and the resulting temperature change

$$C = \frac{dQ}{dT} \tag{19.1}$$

**specific heat**

where $dQ$ is the energy required to produce a $dT$ temperature change. Ordinarily, heat capacity is specified per mole of material (e.g., J/mol·K, or cal/mol·K). **Specific heat** (often denoted by a lowercase $c$) is sometimes used; this represents the heat capacity per unit mass and has various units (J/kg·K, cal/g·K, Btu/lb$_m$·°F).

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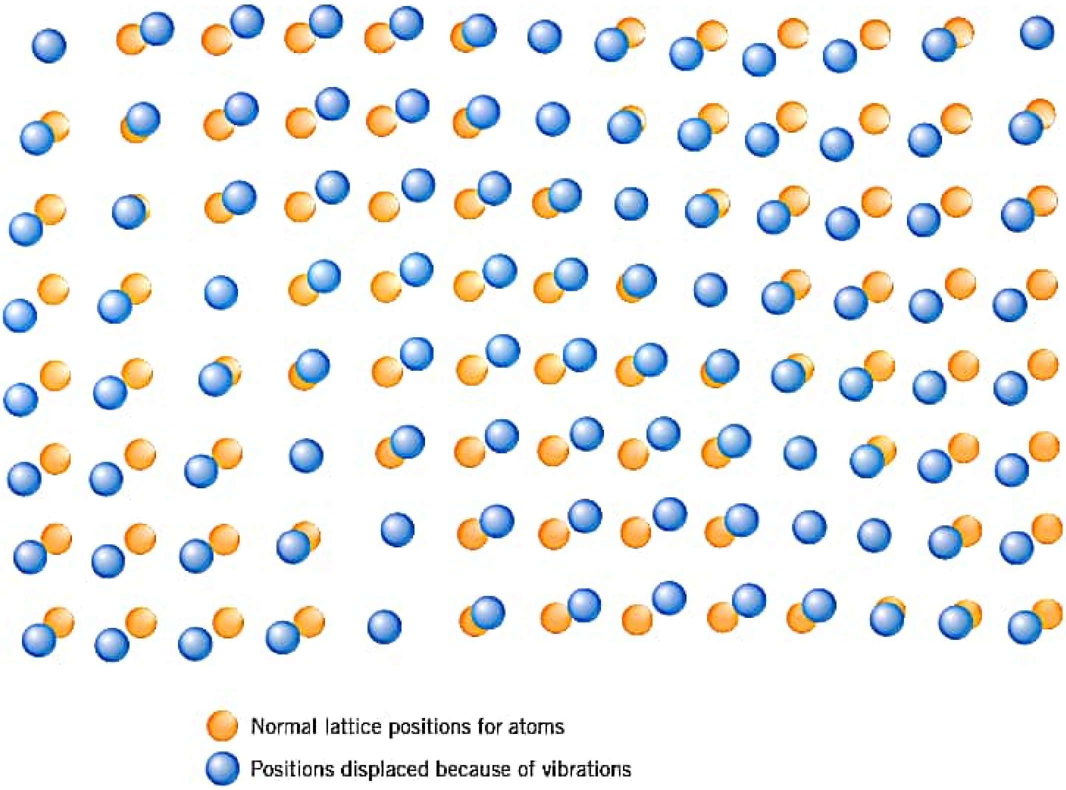

**Figure 19.1** Schematic representation of the generation of lattice waves in a crystal by means of atomic vibrations. (Adapted from "The Thermal Properties of Materials" by J. Ziman. Copyright © 1967 by Scientific American, Inc. All rights reserved.)

There are really two ways in which this property may be measured, according to the environmental conditions accompanying the transfer of heat. One is the heat capacity while maintaining the specimen volume constant, $C_v$; the other is for constant external pressure, which is denoted $C_p$. The magnitude of $C_p$ is almost always greater than $C_v$; however, this difference is very slight for most solid materials at room temperature and below.

## Vibrational Heat Capacity

**phonon**

In most solids the principal mode of thermal energy assimilation is by the increase in vibrational energy of the atoms. Again, atoms in solid materials are constantly vibrating at very high frequencies and with relatively small amplitudes. Rather than being independent of one another, the vibrations of adjacent atoms are coupled by virtue of the atomic bonding. These vibrations are coordinated in such a way that traveling lattice waves are produced, a phenomenon represented in Figure 19.1. These may be thought of as elastic waves or simply sound waves, having short wavelengths and very high frequencies, which propagate through the crystal at the velocity of sound. The vibrational thermal energy for a material consists of a series of these elastic waves, which have a range of distributions and frequencies. Only certain energy values are allowed (the energy is said to be *quantized*), and a single quantum of vibrational energy is called a **phonon**. (A phonon is analogous to the quantum of electromagnetic radiation, the *photon*.) On occasion, the vibrational waves themselves are termed phonons.

The thermal scattering of free electrons during electronic conduction (Section 18.7) is by these vibrational waves, and these elastic waves also participate in the transport of energy during thermal conduction (see Section 19.4).

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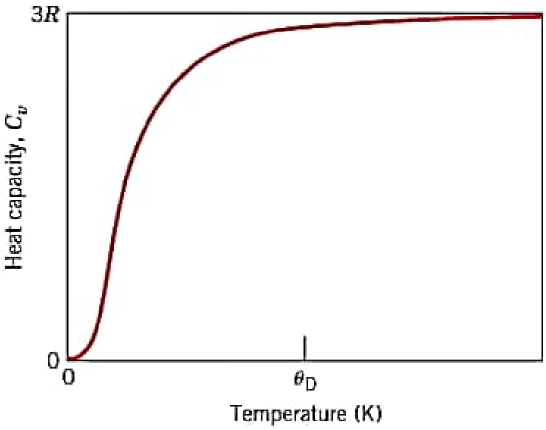

**Figure 19.2** The temperature dependence of the heat capacity at constant volume; $\theta_D$ is the Debye temperature.

## Temperature Dependence of the Heat Capacity

The variation with temperature of the vibrational contribution to the heat capacity at constant volume for many relatively simple crystalline solids is shown in Figure 19.2. The $C_v$ is zero at 0 K, but it rises rapidly with temperature; this corresponds to an increased ability of the lattice waves to enhance their average energy with ascending temperature. At low temperatures the relationship between $C_v$ and the absolute temperature $T$ is

Dependence of heat capacity (at constant volume) on temperature, at low temperatures (near 0 K)

$$C_v = AT^3 \tag{19.2}$$

where $A$ is a temperature-independent constant. Above what is called the *Debye temperature* $\theta_D$, $C_v$ levels off and becomes essentially independent of temperature at a value of approximately 3$R$, $R$ being the gas constant. Thus, even though the total energy of the material is increasing with temperature, the quantity of energy required to produce a one-degree temperature change is constant. The value of $\theta_D$ is below room temperature for many solid materials, and 25 J/mol·K is a reasonable room-temperature approximation for $C_v$. Table 19.1 presents experimental specific heats for a number of materials; $c_p$ values for still more materials are tabulated in Table B.8 of Appendix B.

## Other Heat Capacity Contributions

Other energy-absorptive mechanisms also exist that can add to the total heat capacity of a solid. In most instances, however, these are minor relative to the magnitude of the vibrational contribution. There is an electronic contribution in that electrons absorb energy by increasing their kinetic energy. However, this is possible only for free electrons—those that have been excited from filled states to empty states above the Fermi energy (Section 18.6). In metals, only electrons at states near the Fermi energy are capable of such transitions, and these represent only a very small fraction of the total number. An even smaller proportion of electrons experiences excitations in insulating and semiconducting materials. Hence, this electronic contribution is ordinarily insignificant, except at temperatures near 0 K.

Furthermore, in some materials other energy-absorptive processes occur at specific temperatures—for example, the randomization of electron spins in a ferromagnetic material as it is heated through its Curie temperature. A large spike is produced on the heat-capacity-versus-temperature curve at the temperature of this transformation.

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**Table 19.1 Tabulation of the Thermal Properties for a Variety of Materials**

| *Material* | $c_p$ (J/kg·K)[a] | $\alpha_l$ $[(°C)^{-1} \times 10^{-6}]$[b] | $k$ (W/m·K)[c] | $L$ $[\Omega \cdot W/(K)^2 \times 10^{-8}]$ |
|---|---|---|---|---|
| ***Metals*** | | | | |
| Aluminum | 900 | 23.6 | 247 | 2.20 |
| Copper | 386 | 17.0 | 398 | 2.25 |
| Gold | 128 | 14.2 | 315 | 2.50 |
| Iron | 448 | 11.8 | 80 | 2.71 |
| Nickel | 443 | 13.3 | 90 | 2.08 |
| Silver | 235 | 19.7 | 428 | 2.13 |
| Tungsten | 138 | 4.5 | 178 | 3.20 |
| 1025 Steel | 486 | 12.0 | 51.9 | — |
| 316 Stainless steel | 502 | 16.0 | 15.9 | — |
| Brass (70Cu–30Zn) | 375 | 20.0 | 120 | — |
| Kovar (54Fe–29Ni–17Co) | 460 | 5.1 | 17 | 2.80 |
| Invar (64Fe–36Ni) | 500 | 1.6 | 10 | 2.75 |
| Super Invar (63Fe–32Ni–5Co) | 500 | 0.72 | 10 | 2.68 |
| ***Ceramics*** | | | | |
| Alumina ($Al_2O_3$) | 775 | 7.6 | 39 | — |
| Magnesia (MgO) | 940 | 13.5[d] | 37.7 | — |
| Spinel ($MgAl_2O_4$) | 790 | 7.6[d] | 15.0[e] | — |
| Fused silica ($SiO_2$) | 740 | 0.4 | 1.4 | — |
| Soda–lime glass | 840 | 9.0 | 1.7 | — |
| Borosilicate (Pyrex) glass | 850 | 3.3 | 1.4 | — |
| ***Polymers*** | | | | |
| Polyethylene (high density) | 1850 | 106–198 | 0.46–0.50 | — |
| Polypropylene | 1925 | 145–180 | 0.12 | — |
| Polystyrene | 1170 | 90–150 | 0.13 | — |
| Polytetrafluoroethylene (Teflon) | 1050 | 126–216 | 0.25 | — |
| Phenol-formaldehyde, phenolic | 1590–1760 | 122 | 0.15 | — |
| Nylon 6,6 | 1670 | 144 | 0.24 | — |
| Polyisoprene | — | 220 | 0.14 | — |

[a] To convert to cal/g·K, multiply by $2.39 \times 10^{-4}$; to convert to $\text{Btu/lb}_\text{m}$·°F, multiply by $2.39 \times 10^{-4}$.

[b] To convert to $(°F)^{-1}$, multiply by 0.56.

[c] To convert to cal/s·cm·K, multiply by $2.39 \times 10^{-3}$; to convert to Btu/ft·h·°F, multiply by 0.578.

[d] Value measured at 100°C.

[e] Mean value taken over the temperature range 0–1000°C.

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### 3.3 Debye Theory

The next advance in the theory of specific heat began with the suggestion of Madelung and Sutherland that the Einstein frequency is equivalent not only to the infrared absorption frequency of the crystal but also to the frequency of the shortest lattice vibration which can propagate through crystal. This wave has a wavelength of about twice the interatomic distance. Since waves of longer wavelength can also propagate through the crystal, Madelung made the further suggestion that a whole spectrum of frequencies should be used in computing $C_v$ rather than just the single frequency $\omega_E$.

Debye made two assumptions: *(i)* that the solid is a continuous medium and *(ii)*, that the total number of waves is equal 3N, where N is the number of atoms in the crystal. This assumption implies that the solid is not really continuous after all and that the shortest permissible wavelengths are those of about two interatomic distances. The restriction is expressed mathematically as

$$\int_0^{w_D} \rho(\omega)\ d\omega = 3N \tag{7}$$

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where $\rho(\omega)\ d\omega$ is the number of waves (or modes) with frequencies between $\omega$ and $\omega + d\omega$ is solid. The energy associated with each of these waves is that of a Planck oscillator, so that one obtains for the total energy, $E$,

$$E = \int_0^\infty \frac{\rho(\omega)\ \hbar\omega d\omega}{e^{\hbar\omega/kT} - 1} \tag{8}$$

$\rho(\omega)$ is computed in a manner analogous to that employed in black body radiation, resulting in

$$\rho(\omega) = \frac{V}{2\pi^2}\left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right)\omega^2 \tag{9}$$

where $v_l$ is the velocity of longitudinal sound waves, $v_t$ that of transverse waves and $V$ the volume of the solid.

The Debye frequency $\omega_D$ is the maximum allowable frequency. Thus for $\omega > \omega_D$, $\rho(\omega)$ is zero and the value of integral in Eq. (7) above this limiting frequency is zero. This allows the upper limit in Eq. (8) to be replaced by $\omega_D$. It is customary to replace the Debye frequency $\omega_D$ by the Debye characterisitc temperature $\theta_D$, defined by the relation

$$k\theta_D = \hbar\omega_D \tag{10}$$

Finally Debye obtained the expression for specific heat as

$$C_v = 9R\left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} \frac{e^x\ x^4}{(e^x - 1)^2}\,dx \tag{11}$$

with $x = \hbar\omega/k_BT$. As $T$ approaches infinity, i.e. for $x_D << 1$, $C_v \approx 3R$. We thus obtain the Debye classical $T^3$ law results. At low temperatures for $T << \theta_D$, the upper limit goes to infinity. Then the integral in Eq. (11) is equal to $4\pi^4/15$. Hence

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

Thus $C_v$ varies as $T^3$ as observed experimentally. Figure 13.3 shows a plot of $C_v/3R$ versus $T/\theta_D$ as given by the Debye theory. The experimental results for many materials fit a single curve.

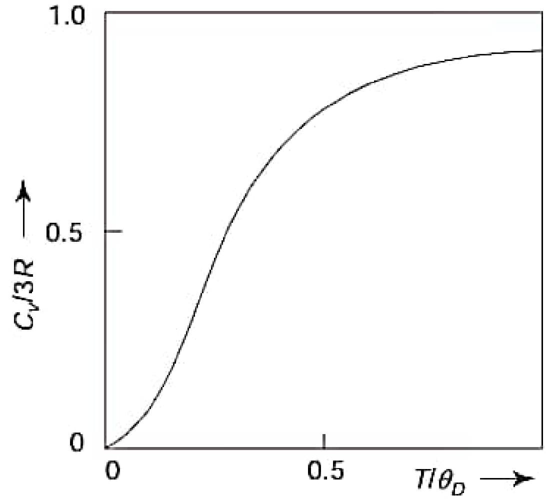

**Fig. 13.3 Debye specific heat curve**

The courses of the two curves shown in Figs. 13.1 and 13.3 are quite similar for $T$ above about 0.2 $\theta_D$. The critical test distinguishing between two theroies must therefore be made at temperatures below about 0.1 $\theta_D$, where the Debye $T^3$ should hold. This $T^3$ law failed for metals. The reason for this failure is now understood, for Sommerfeld's theory of metals shows that the conduction electrons can make an important contribution to the heat capacity.

According to Sommerfeld, there must be a linear term in the temperature in the expression for $C_v$ in order to account for the electron contribution. Thus, we obtain

$$C_v = \gamma T + \left(\frac{12\pi^4\ R}{5}\right)\left(\frac{T}{\theta_D}\right)^3 \tag{13}$$

The coefficient $\gamma$ in the electron term is sometimes called the Sommerfeld gamma. To analyse low temperature $C_v$ data for metals, $C_v/T$ versus $T^2$ is plotted. According to Eq. (13) this should give a straight line of slope $12\pi^4\ R/5\theta_D^3$ and of intercept $\gamma$ on the $C_v/T$ axis.

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## 16. THERMOELECTRICITY

This implies direct conversion of heat into electricity. If an electric circuit is made by connecting two dissimilar metals and the junctions of the two metals are kept at different temperatures, a current flows in the circuit in a direction depending on the temperature difference between the two junctions and the nature of metals. This effect is known as *Seeback effect* after the name of the discoverer, Seeback. The electric current is called the *thermoelectric current* and is the result of an e.m.f. in the circuit caused by the temperature difference between the junctions. This e.m.f. is termed as *thermo e.m.f.* The circuit formed by the two different metals whose junctions are at two different temperatures is known as *thermocouple* (Fig. 5.18).

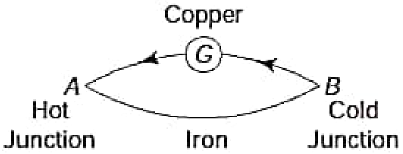

**Fig. 5.18 Thermocouple**

When the two junctions of a couple are $T\,K$ and the temperature of one junction is raised by a differential $dT$, causing a thermo E.M.F. $dE$ in the circuit, the thermoelectric power of the two metals at temperature $T$ is defined by

$$P = \left.\frac{dE}{dT}\right|_T \tag{29}$$

The temperature of the hot junction at which the thermo e.m.f. or the thermoelectric current attain maximum is called the neutral temperature $t_n$ for the given couple. The temperature of the hot junc where the thermo e.m.f. or the current is zero and changes direction, is termed as the *inversion temperature* $t_I$. The inversion temperature is as much above the neutral temperature as the cold junction is below it

$$t_n = \frac{t_c + t_I}{2} \tag{30}$$

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where $t_c$ is the temperature of the cold junction. The variation of the thermo e.m.f. with the temperature of the hot junction is shown in Fig. 5.19. The nature of the curve is the same for any pair of metals in the Seeback series (Bi, Ni, Co, Pd, Pt, U, Cu, Mn, Ti, Hg, Pb, Sn, Cr, Mo, Rh, Ir, Au, Ag, Zn, W, Cd, Fe, As, Sb, Te); the numerical values will however will be different for different couples. In most of the cases, the curve of Fig. 5.19 represent a parabola to a first approximation.

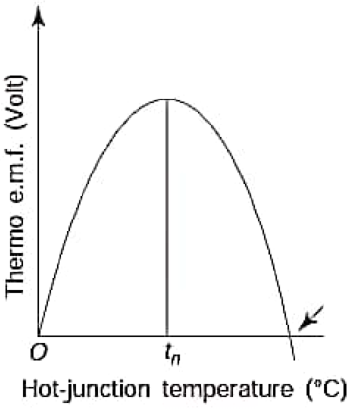

**Fig. 5.19** **Variation of the thermo e.m.f. with the temperature of the hot junction**

## 17. ORIGIN OF THE THERMOELECTRIC EFFECT

One can explain the origin of the thermoelectric effect with the help of the free electron theory. A conductor possesses a large number of free electrons, the concentration of which is different for different metals. When the wires of two different metals are placed in contact with each other, the electrons diffuse one metallic wire to another metallic wire because of the concentration difference (i.e. gradient). As a result of this, one of the metallic wire becomes positively charged and the other negatively charged. This results in a setting up of a potential difference across the contact. This is termed as *contact potential.* We must note that the contact potential is strongly affected by the temperature. When one of the junctions of the thermocouple is heated (keeping the other junction cold), the potential difference set up at the hot junction is comparatively more than that of the cold junction. As a result of this, a net e.m.f. is produced in the thermocouple and called as thermo e.m.f. The thermo e.m.f. is the cause of thermoelectric current.

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