

1. Basic Concepts and Definitions

1.1. Definition of Specific Heat

The specific heat of a system is defined as the quantity of heat required to raise a unit mass of the system by one degree in temperature. Thus, if the heat is dQ and the rise in temperature is dT , the specific heat may be expressed by the following limit:

$$C_{x,y,\dots} = \lim_{dT \rightarrow 0} \left(\frac{dQ}{dT} \right)_{x,y,\dots} \quad (1.1)$$

where x, y, \dots , are the quantities such as pressure, volume, magnetic field and so on, that are kept constant during the measurement.

In general specific heat depends upon the temperature of the system and the way it is heated. The two principal specific heats are c_v and c_p . The former refers to measurements made at constant volume and the latter to those made under constant pressure. By convention (c) is used for the specific heat per unit mass and (C) for one mole of the substance. In most theoretical calculations it is the specific heat per mole that is computed since it refers to a fixed number of particles. This quantity is sometimes referred to as *heat capacity*. The heat capacities corresponding to c_v and c_p , therefore, are commonly indicated by C_v and C_p , respectively. For the most part results will be given for one mole of the material. It will be clear from the context whether specific heat per mole or per unit mass is meant.

In recent years the SI system of units has become increasingly used in scientific literature to express values of specific heat. In this system c_v or c_p are expressed in J/kg.K and C_v or C_p in J/mol.K. In engineering literature, however, it is still common to find the specific heats expressed in BTU/lb.deg.F. This has almost the same value as the earlier unit cal/g.K, now no longer in use.

1.2. Thermodynamic Relations

Almost all thermodynamic quantities may be expressed in terms of temperature T , volume V , pressure P and entropy S , the very same quantities that enter the expressions of heat and work. Hence all processes involving heat and work are

governed by the fundamental laws of thermodynamics. It is pertinent then, to review here the basic thermodynamic relations. To do this we shall consider the case of a simple system such as an ideal gas. When such a gas is given a small quantity of heat dQ , part of it goes to increase the internal energy of the system, the remainder being used by the system to perform external work. Thus:

$$dQ = dE - dW \quad (1.2)$$

where dE is the change in the internal energy and dW represents the work done. We use the convention that $dW > 0$ if work is done on the system and $dW < 0$ if the system itself performs work. Similarly $dQ > 0$ if heat is added to the system and $dQ < 0$ if heat is lost by the system.

For a quasi-static reversible process between two equilibrium states if heat is absorbed or expelled by the system over a small portion of the path for which the temperature of the system is T , then the change in its entropy is given by following relation:

$$dQ = TdS \quad (1.3)$$

For an ideal fluid (liquid or gas) the pressure is the same in every direction at any given point. Any work associated with a change in volume, therefore, is of the form:

$$dW = -PdV \quad (1.4)$$

Equation (1.2) may now be written as:

$$dE = TdS - PdV \quad (1.5)$$

dE is a perfect differential since the internal energy depends only on the initial and final states of that system and not on the path it takes.

The state of a system may be described by the relationship between its volume V , its temperature T , and its pressure P . Any relationship between these three quantities is referred to as the *equation of state* and is formulated as:

$$f(P, V, T) = 0 \quad (1.6)$$

Thus, any one of P , V or T may be expressed in terms of the other two. More relevant here is the fact that only two of these three quantities may be varied

arbitrarily at the same time. Hence, when temperature is varied either P or V can be kept constant, but not both. Consequently, as has already been mentioned, there are two principal heat capacities namely C_v and C_p . The heat capacity at constant volume defined by:

$$C_v = \left(\frac{dQ}{dT} \right)_v = T \left(\frac{\partial S}{\partial T} \right)_v \quad (1.7)$$

is the quasi-static heat flow per mole required to raise the temperature of the system by a unit degree when the volume and the number of particles are kept constant. Similarly, the heat capacity at constant pressure is given by:

$$C_p = \left(\frac{dQ}{dT} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p \quad (1.8)$$

again with the understanding that the process is quasi-static and that the pressure and the number of particles are held constant during the process.

The fact that Eq. (1.5) is an exact differential suggests that the quantities T , S , P and V appearing on the right hand side must be interrelated to ensure this condition. To obtain this relationship use is made of the fact that the second derivative of E must be independent of the order of differentiation. Thus referring to Eq. (1.5), $\partial^2 E / \partial V \partial S = \partial^2 E / \partial S \partial V$ and hence:

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V \quad (1.9)$$

This is one of a set of useful relations known as *Maxwell's relations*. In certain cases it is often more convenient to introduce other principal thermodynamic functions; namely the Enthalpy H , the Helmholtz free energy F and the Gibbs' free energy G . Of these, as we shall see, the Helmholtz free energy is particularly useful when discussing the statistical thermodynamics of a system of particles or modes. These three functions are the partial Legendre transforms of E and are, therefore, measures of the energy content of the system under various conditions (see e.g Callen [1], Chapter 5 for details). Hence in reversible thermodynamic processes their changes:

$$dH = d(E + PV) = TdS + VdP \quad (1.10)$$

$$dF = d(E - TS) = -SdT - PdV \quad (1.11)$$

$$dG = d(E - TS + PV) = -SdT + VdP \quad (1.12)$$

must depend only on the initial and final states of the system, i.e. they are exact differentials. From this fact the remaining three Maxwell's relations involving S , T , P and V are obtained in the same way as above. For convenience we give here all four relations comprising these parameters.

$$\begin{aligned} \left(\frac{\partial V}{\partial S}\right)_p &= \left(\frac{\partial T}{\partial P}\right)_S & \left(\frac{\partial S}{\partial P}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_p \\ \left(\frac{\partial P}{\partial T}\right)_v &= \left(\frac{\partial S}{\partial V}\right)_T & \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_v \end{aligned} \quad (1.13)$$

Maxwell's relations have been discussed by a number of authors [1,2,3]. Of these Callen [1] is particularly recommended as he deals with the topic in great detail.

1.3. Relationship Between C_p and C_v

Maxwell's relations, which hold good for reversible processes, are useful in expressing thermodynamic formulas in terms of experimentally measurable quantities. As an illustration of their use we shall derive the difference between the two principal heat capacities C_p and C_v . For the sake of simplicity we shall again restrict our discussion to the familiar case of gases since C_p and C_v of solids obey the same thermodynamic relations as those of liquids and gases (see e.g. Viswanathan and Gopal [4]), provided that the only stress is a hydrostatic pressure and not, for example, a shear.

Consider the entropy of one mole of a substance as a function of T and P . Then:

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial P}\right)_T dP \quad (1.14)$$

from which:

$$\left(\frac{\partial S}{\partial T}\right)_v = \left(\frac{\partial S}{\partial T}\right)_p + \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_v \quad (1.15)$$

Multiplying both sides by T , and recalling the definitions of C_p and C_v , leads to:

$$C_v = C_p + T \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_v \quad (1.16)$$

Using the Maxwell relation $(\partial S/\partial P)_T = -(\partial V/\partial T)_p$ the above equation may be written as:

$$C_p - C_v = T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial P}{\partial T}\right)_v \quad (1.17)$$

This relationship is general, that is, it is valid for any substance and involves known or measurable quantities if the equation of state is known explicitly. For instance, for n -moles of an ideal gas, for which $PV = nRT$, where $R = 8.3143\text{J/mol.K}$ is the gas constant, Eq. (1.17) gives the familiar relation $C_p - C_v = nR$. The same relationship applies equally well to the non-ideal gases, but only at low pressures.

We now take the volume as a function of P and T and write:

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial P}\right)_T dP \quad (1.18)$$

For a process at constant volume $dV = 0$, and hence:

$$0 = \left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_v \quad (1.19)$$

from which:

$$\left(\frac{\partial P}{\partial T}\right)_v = -\left(\frac{\partial V}{\partial T}\right)_p / \left(\frac{\partial V}{\partial P}\right)_T \quad (1.20)$$

Combining this with Eq. (1.17), and recalling the definition of the volume expansion coefficient $\beta = V^{-1}(\partial V/\partial T)_p$ and the isothermal compressibility $\kappa_T = -V^{-1}(\partial V/\partial P)_T$, one arrives at:

$$C_p - C_v = \frac{V\beta^2}{\kappa_T} T \quad (1.21)$$

This relation, often referred to as the *dilation* contribution to the measured specific heat is a general expression and applies to both solids and liquids.

The isothermal compressibility is a positive quantity and hence C_p is always greater than C_v . However, the difference $(C_p - C_v)$ goes to zero as $T \rightarrow 0$. To see this, consider the Maxwell relation $(\partial S/\partial P)_T = -(\partial V/\partial T)_p$. The third law of thermodynamics suggests that as $T \rightarrow 0$ the absolute magnitude of the entropy of any material in thermal equilibrium approaches a constant limiting value, independent of all parameters. Therefore, $(\partial S/\partial P)_T$, and hence β , goes to zero as $T \rightarrow 0$. Consequently $C_p \rightarrow C_v$ in this limit.

The specific heat data are usually obtained under constant, generally atmospheric, pressure since very large pressures are required to keep the volume of a solid constant. However, at temperatures below about 30K the thermal expansion of solids is very small and the difference between C_p and C_v is negligible. For Pd, for instance, $(C_p - C_v)/C_p = 0.03\%$ at $T = 30\text{K}$ [5], while for Al and Cu Giauque and Meads [6] reported no difference at all between C_p and C_v for temperatures up to about 50K. Indeed the ratio $(C_p - C_v)/C_p$ is usually only about 0.1% at $\Theta_D/6$, where Θ_D is the Debye temperature. This ratio rises to about 1% at $\Theta_D/3$, reaching its maximum value at the melting temperature of the solid where it can be as large as 10%. Thus, at temperatures less than about $\Theta_D/6$ effectively it is C_v that is being measured and no correction need be carried out on C_p . At higher temperatures the correction must be made to obtain C_v but this is not always possible because, in addition to a detailed knowledge of the variation of C_p with temperature, the computation of $C_p - C_v$ requires a considerable body of data about the solid under consideration: temperature variation of the molar volume, isothermal compressibility and the volume expansion coefficient. Although thermal expansion data over a wide temperature range are available for many solids, experimental values of compressibility, if known at all, are generally restricted to near room temperature only. In practice, therefore, approximate relations are generally used, the most successful being the *Nernst–Lindemann relation*:

$$C_p - C_v = A C_p^2 T \quad (1.22)$$

where $A = V^2/C_p^2 \kappa_T$ is taken as a constant. Its value is usually computed at room temperature, where data about κ_T is more readily available, and is then used to calculate $C_p - C_v$ over the whole temperature range of interest.

It has been found experimentally that A is indeed nearly constant over a wide range of temperatures. For copper, for instance, the value of A is 4.0×10^{-6} mol./J at $T = 100\text{K}$ and 3.9×10^{-6} mol./J at $T = 800\text{K}$. Similarly, for tungsten the value of A was found to vary only between 3.5×10^{-6} mol./J and 3.6×10^{-6} mol./J for temperatures between 100–1300K. This remarkable constancy of A permits a reasonable estimate of $C_p - C_v$ to be made over a wide temperature range. Unfortunately at present data exist for only a few metals, for which the values of A are listed in Table 1.1.

Table 1.1. Mean value of A (in 10^{-6} mol./J) for some metals.

Element	Al ⁺	Ag ⁺	Cu [*]	Pb ⁺	Pd [◆]	W ^x
T (K)	15-300	15-300	100-800	15-300	30-300	100-1300
A	5.32	5.21	(3.95 ± 0.05)	8.24	2.80	(3.55 ± 0.05)

(+) Giauque and Meads [6]
 (*) Chang and Hultgren [7]
 (◆) Pal [8]
 (x) Singh and Verma [9]

In addition to Eq. (1.21) there is a further relationship between C_p and C_v . It may be shown (see Problem-1) that:

$$\frac{C_p}{C_v} = \frac{\kappa_T}{\kappa_S} \quad (1.23)$$

where κ_T is the isothermal compressibility already defined, and $\kappa_S = - (1/V) (\partial V/\partial P)_S$ is the adiabatic compressibility. C_p/C_v is about 1 for solids and liquids, but is somewhat larger for gases: 1.67 for a mono-atomic gas such as helium, 1.4 for a diatomic gas, e.g. nitrogen and 1.3 for the polyatomic gases.

Equation (1.23), which relates the elastic and calorimetric parameters of a given substance may, at first sight, appear surprising. However, when it is noted that

the C 's are determined under definite conditions of P and V and the κ 's under definite conditions of T and S , the result is not so unexpected. The four quantities P , V , T and S , appearing in E , F , G and H and are linked through Maxwell's relations.

An expression similar to Eq. (1.21) also exists between the elastic parameters κ_T and κ_S and the calorimetric parameter C_p (see e.g. Callen [1], Chapter 3):

$$\kappa_T - \kappa_S = \frac{V\beta^2}{C_p} T \quad (1.24)$$

The specific heat of a system depends, of course, on its temperature. It also depends to a certain extent on the state of the system. For a given temperature T , for example, C_p and C_v change, among other variables, with V and P respectively. Using the Maxwell's relations it is easy to show that:

$$\left(\frac{\partial C_v}{\partial V} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_v \quad (1.25)$$

$$\left(\frac{\partial C_p}{\partial P} \right)_T = -T \left(\frac{\partial^2 V}{\partial T^2} \right)_p$$

These relations confirm that the heat capacities are not completely independent of the equations of state. For instance, while the dependence of C_v on T may be obtained from measurements, for its dependence on other parameters, such as the volume V , one must resort to the equation of state.

The above relations may be generalised to include magnetisation and applied field (see e.g. Morse [3] Chap. 8). We shall make use of them in Chap. 4 when discussing the magnetic specific heats C_M and C_H .

1.4. Third Law of Thermodynamics, Entropy and Specific Heat

It is commonly known that the removal of heat from a substance lowers its temperature except when it undergoes a first order phase transition or a chemical reaction. Given the equivalence of heat and energy it is only natural to conclude that

absolute zero temperature will be reached when the energy of the system is zero. However, the quantum mechanical ground state energy of a system is seldom zero. As we shall see in Chap. 2, a harmonic oscillator, for instance, has a ground state energy $\epsilon_0 = \frac{1}{2}\hbar\omega$, where $\hbar = 1.05459 \times 10^{-34}$ J·s is the Planck constant divided by 2π and ω is the angular frequency of the oscillator. Similarly, the ground state energy per particle of a Fermi gas is $\epsilon_0 = (3/5)k_B T_F$, where $k_B = 1.38062 \times 10^{-23}$ J/K is the *Boltzmann constant* and T_F is the *Fermi temperature*, to be introduced in Chap. 3. However, according to the third law of thermodynamics, the quantity that does in fact fall to zero as the absolute zero temperature is approached is the change in entropy ΔS (but not necessarily its absolute value – see above).

The third law of thermodynamics has important implications for low temperature specific heat. From Eq. (1.3), with $dQ = C_v dT$, one may write for the entropy change between the temperatures T_0 and T :

$$S(T) - S(T_0) = \int_{T_0}^T \left(\frac{C_v}{T} \right) dT \quad (1.26)$$

If we now set $S(T_0) = 0$ at $T_0 = 0$ then the entropy between the absolute zero temperature and a given temperature T is:

$$S(T) = \int_0^T \left(\frac{C_v}{T} \right) dT \quad (1.27)$$

Since $S(T) \rightarrow 0$ as $T \rightarrow 0$, $(C_v/T) \rightarrow \text{constant}$ (or zero), implying that $C_v \rightarrow 0$ as $T \rightarrow 0$. Thus it is sufficient to measure C_v to a low-enough temperature from where it may be safely extrapolated to zero. Although it is clear that the lower the temperature the more accurate the extrapolation and hence the value of $S(T)$, there is no way of knowing exactly how low this temperature should be since in this regard the laws of thermodynamics offer no indication. While for some simple materials measurements down to liquid helium temperature may be adequate, in others the lower limit can be down to the millikelvin range.

We shall see in the following chapters that the low temperature specific heat of a simple system is of the form $C = \gamma T + \beta_3 T^3$. For such systems, therefore, a graph of C/T against T^2 should be a straight line with the intercept γ and slope β_3 . Fig. 1.1 shows this for Cu. The temperature dependence of C for an ordinary solid is thus, simple enough in principle to permit a ready extrapolation to $T = 0$ K. However, even for such solids this is not straightforward since in practice what is

measured is not C_v but C_p and at temperatures where the difference $C_p - C_v$ is significant, data need to be corrected for C_v using Eq. (1.21). Only then can the extrapolation be carried out with confidence.

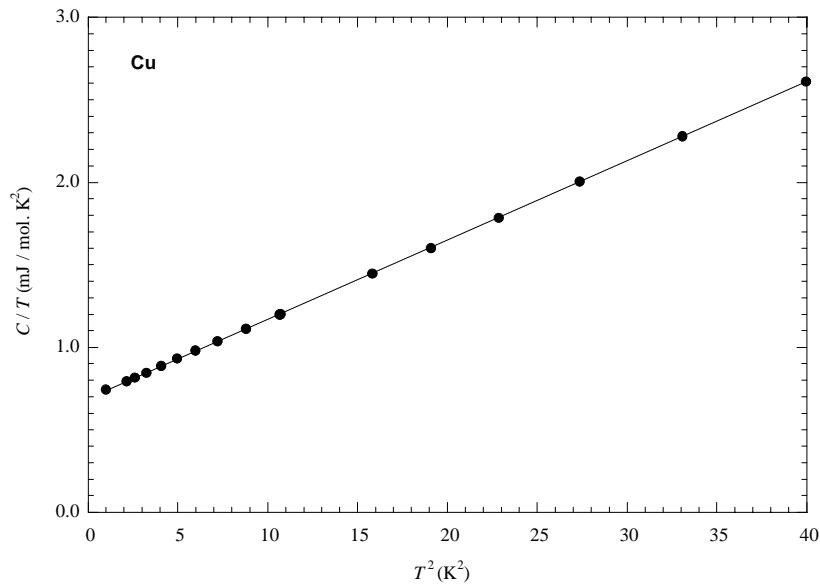


Figure 1.1. C/T against T^2 for Cu (data from Osborne *et al.* [10]).

The specific heat of some solids shows complex behaviour, Fig. 1.2. As we shall see in Chap. 6, this may be due to magnetic or structural phase transitions, spin re-orientations, or to electronic or nuclear excitations to higher energy levels. In such cases there is no way of knowing the temperature variation of the specific heat outside the range of actual measurements and the use of thermodynamics is not sufficient to explain the observed behaviours. For this reason the methods of Statistical Mechanics are used. This technique, the basic concepts of which are introduced below, will be employed extensively in the following chapters.

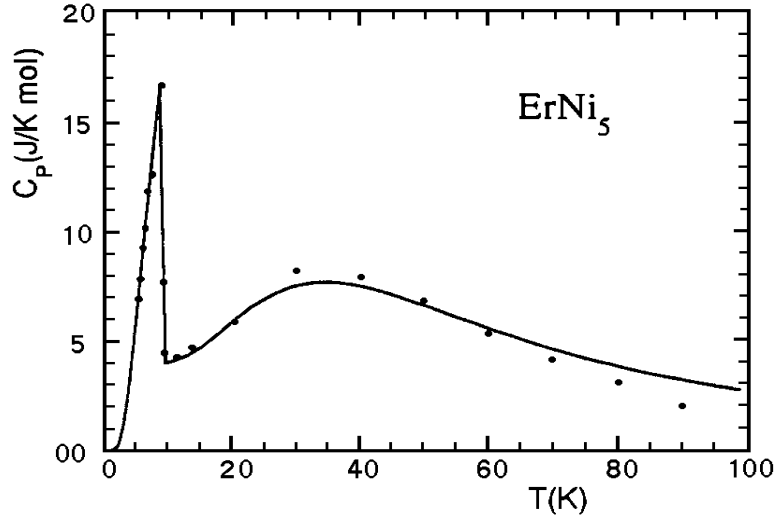


Figure 1.2. Temperature variation of the specific heat of the compound ErNi_5 (after Zhang *et al.* [11]. Reproduced with permission from Elsevier Science).

1.5. Statistical Treatment of Specific Heat

The specific heat of a solid, which involves a large number of particles (nuclei, atoms, molecules etc.), is determined by the ways in which its internal energy is distributed among its various modes of excitation. The interaction between these particles, or of the particles with an external agent such as a magnetic field may be analysed using an appropriate theoretical model to determine the various energy levels, ε_i , accessible to the system. Once this has been done the computation of the relevant thermodynamic quantities is readily obtained from the partition function:

$$Z = \sum_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right) \quad (1.28)$$

where the summation is over all the allowed states of the system. The quantities of interest to us here can be computed from the Helmholtz free energy:

$$F = -k_B T \ln Z \quad (1.29)$$

once Z has been determined since:

$$E = k_B T^2 \left(\frac{\partial \ln Z}{\partial T} \right)_v$$

$$S = - \left(\frac{\partial F}{\partial T} \right)_v \quad (1.30)$$

and

$$C_v = T \left(\frac{\partial S}{\partial T} \right)_v = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_v$$

Thus the specific heat at constant volume can be computed from the temperature dependence of either the internal energy or the Helmholtz free energy. The choice will depend on the nature of the theoretical model chosen.

The above equations show that the quantity that arises naturally from computations is the specific heat at constant volume. However, as was remarked above, for solids C_p is normally measured and the necessary corrections to obtain C_v are then made using Eq. (1.21).

In addition to excitations to discrete energy levels, particles in a solid undergo translational and vibrational motions. In a gas one has, in addition, a rotational motion. It is reasonable to assume that the energy associated with each of these is independent of the others, in which case the partition function factors out with respect to the various modes:

$$Z = Z_{tr} Z_{vib} Z_{rot} Z_{el} \quad (1.31)$$

This assumption is not strictly rigorous. In a gas, for instance, the vibration of a polyatomic molecule changes the instantaneous inter-atomic distance, thereby changing the moment of inertia of the rotating molecule. But, since the vibrations are generally very fast compared to the rotations, the above assumption regarding these two modes of excitations remains justifiable.

As F involves $\ln Z$, which is the sum of $\ln Z_{tr}$, $\ln Z_{vib}$, etc., the overall thermodynamic quantity of a given system is the sum of the contributions of various modes. Some of these modes are excited over the entire temperature range, others

only over a restricted interval. Thus, while each contributes to the specific heat the form of the observed specific heat depends on the way these modes vary within the temperature range of measurements. We shall find ample examples of this in the following chapters.

1.6. Degrees of Freedom and the Law of Equipartition

Consider a molecule consisting of N atoms and assume that they are point masses. This is a reasonable supposition since the nuclear radius is much smaller than the ionic or molecular radii. In order to determine the instantaneous position of the atoms in space we require $3N$ coordinates. These are not necessarily Cartesian; depending on the nature of the problem a more suitable coordinate system may be chosen. Whatever the preferred system, the number of independent coordinates needed to determine the position of all the atoms in the molecule is called the number of its *degrees of freedom*.

The translational motion of the molecule as a whole can be represented by the motion of its centre of mass. Three coordinates or degrees of freedom are needed to determine its position in space. The remaining $(3N - 3)$ coordinates represent the *internal degrees of freedom* of the system and are further subdivided into rotations and vibrations. A diatomic molecule, for instance, has $(3 \times 2 - 3) = 3$ internal degrees of freedom. Of these two are rotational; the molecule is able to rotate only about the x - and z -axis, say, but not about the y -axis on which the atoms lie. The third is vibrational; when heated the atoms in the molecule vibrate about their equilibrium positions. In both types of motion the energy has a quadratic form. Thus the total energy is a sum of quadratic terms, each arising from a degree of freedom of the system which, according to the law of equipartition, contributes $\frac{1}{2}k_B T$ to the energy of the molecule.

To clarify the matter further, consider a diatomic molecule of mass m_1 and m_2 separated by a mean distance r as shown in Fig. 1.3(a). If the molecule is viewed as a rigid rotator then its moment of inertia about the x - (or z -) axis is:

$$I = m_1 r_1^2 + m_2 r_2^2 \quad (1.32)$$

and the rotational kinetic energy:

$$E_{\text{rot}} = \frac{1}{2} I \omega^2 \quad (1.33)$$

The distances r_1 and r_2 from the centre of mass are:

$$r_1 = \frac{m_2}{m_1 + m_2} r \quad \text{and} \quad r_2 = \frac{m_1}{m_1 + m_2} r \quad (1.34)$$

leading to:

$$I = \mu r^2 \quad (1.35)$$

where $\mu = m_1 m_2 / (m_1 + m_2)$ is the *reduced mass*. Thus, the rotational motion of the molecule is equivalent to that of a mass μ at a distance r from the origin of the axes. Only two coordinates are needed to describe such a motion completely. Because of the rotational nature of the problem, the angles θ and ϕ , Fig. 1.3(b), are two convenient coordinates to choose and are sufficient to establish the orientation of the rotator in space. Thus there are two degrees of freedom for the rotational motion of a diatomic molecule. Since, according to the law of equipartition, in thermal equilibrium each degree of freedom contributes $\frac{1}{2}k_B T$ to the mean energy of the system, the rotational energy per molecule is $2 \times (\frac{1}{2}k_B T) = k_B T$.

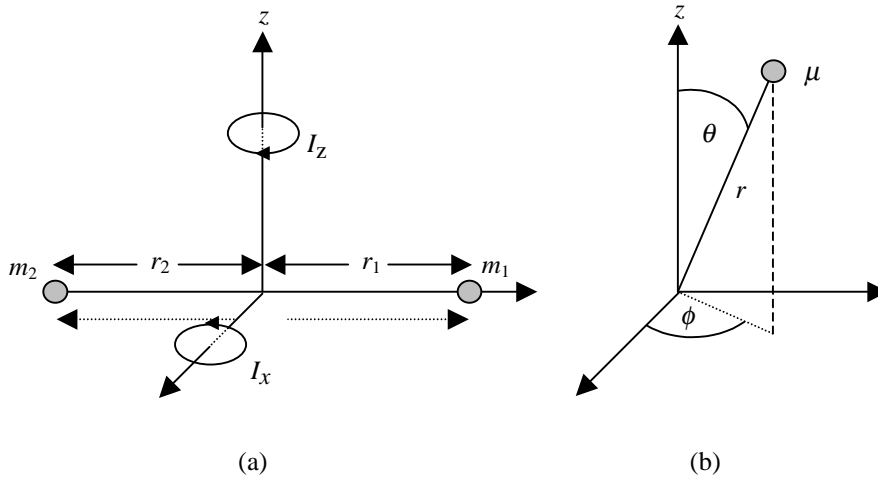


Figure 1.3. (a) Model of a diatomic molecule as a rigid rotator. (b) The rotational motion is equivalent to that of a mass μ at a distance r from the origin of the coordinate system.

The energy associated with the vibrational motion of the molecule is also quadratic in form and is made up of kinetic and potential terms:

$$E_{\text{vib}} = \frac{1}{2} \mu \left(\frac{dx}{dt} \right)^2 + \frac{1}{2} Kx^2 \quad (1.36)$$

where K is the inter-atomic force constant and $x = r - r_0$ is the displacement from the equilibrium position. Thus two variables, x and (dx/dt) , are required to determine the vibrational motion completely.

As was remarked above, on average each quadratic term in energy expression contributes $\frac{1}{2}k_B T$ to the energy of the system. Thus the total average energy of a diatomic molecule is:

$$\langle \varepsilon \rangle = \langle \varepsilon_{\text{tr}} \rangle + \langle \varepsilon_{\text{rot}} \rangle + \langle \varepsilon_{\text{vib}} \rangle = (3/2)k_B T + k_B T + k_B T = (7/2) k_B T \quad (1.37)$$

or $\langle E \rangle = (7/2)RT$ per mole. Note that in the above equation the translational energy $\langle \varepsilon_{\text{tr}} \rangle$ is that of the centre of mass.

A triatomic molecule has $(3 \times 3 - 3) = 6$ internal degrees of freedom. The way in which these are distributed between the vibrational and rotational modes depends on the shape of the molecule. For a *linear molecule* in which the atoms lie on one axis, Fig. 1.4(a), the moment of inertia along this axis is negligible (it is in fact zero for point masses) and hence the number of rotational modes is essentially two. Rotationally such a molecule behaves just like a diatomic molecule, able to rotate about only two axes perpendicular to the line joining the atoms. Thus there remain $6 - 2 = 4$ vibrational degrees of freedom and according to the equipartition law one now has:

$$\langle \varepsilon \rangle = \langle \varepsilon_{\text{tr}} \rangle + \langle \varepsilon_{\text{rot}} \rangle + \langle \varepsilon_{\text{vib}} \rangle = (3/2)k_B T + k_B T + 4k_B T = 6\frac{1}{2}k_B T \quad (1.38)$$

or $\langle E \rangle = 6\frac{1}{2}RT$ per mole.

A triatomic *bent molecule*, Fig. 1.4(b), has three principal moments of inertia and so the number of rotational modes is three, leaving three modes for vibrations. The average energy of the molecule is therefore:

$$\langle \varepsilon \rangle = (3/2)k_B T + (3/2)k_B T + 3k_B T = 6k_B T \quad (1.39)$$

i.e. $\langle E \rangle = 6RT$ per mole. Thus, according to the equipartition principle, a body takes up energy equivalent to $\frac{1}{2}RT$ per mole for each rotational or translational degree of freedom and RT per mole for each vibrational degree of freedom.

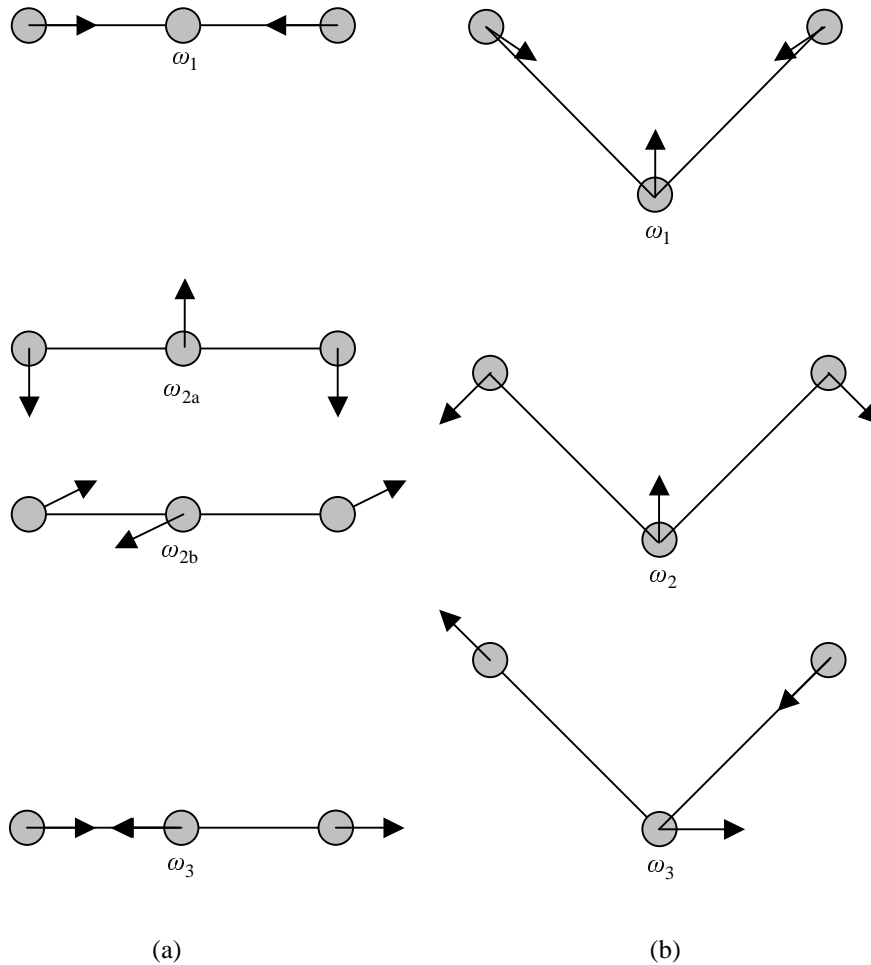


Figure 1.4. (a) The normal modes of vibration of a linear triatomic molecule. Note that while the two stretching modes have different frequencies the two bending vibrations have the same frequency. (b) The three normal modes of vibration of a bent triatomic molecule.

The vibrational motions of atoms coupled together by linear restoring forces are generally quite complex. However, they can be represented by a set of simple

motions entirely independent of each other, called the *normal modes*. When one such mode is excited the remainder are at rest and hence the total vibrational energy of the system is the sum of the energies of the individual modes.

In a normal mode each atom vibrates with the same frequency. An example familiar to all is the vibrating string in which all particles of the string move sinusoidally and have the same frequency. In Fig. 1.4(a) and 1.4(b) the normal vibrational modes of a linear and a bent triatomic molecule, respectively, are displayed. As the figure shows, the bent molecule has three distinct modes but the linear molecule has four, of which the two *bending vibrations* are degenerate in frequency.

Degrees of freedom, normal modes and normal coordinates are discussed in some detail by a number of authors. We cite here Pain [12], Kibble and Berkshire [13] and Moore [14], to which readers may refer for more information.

References

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Problems

1.1. Making use of the reciprocal relation for the partial derivatives given in Appendix 1 obtain the relation given by Eq. (1.23).

1.2. In the high temperature limit the rotational partition function of a homonuclear diatomic molecule is given by:

$$Z_{\text{rot}} = \frac{T}{2\theta_{\text{rot}}} \left[1 + \frac{1}{3} \left(\frac{\theta_{\text{rot}}}{T} \right) + \frac{1}{15} \left(\frac{\theta_{\text{rot}}}{T} \right)^2 + \dots \right]$$

where θ_{rot} is a constant called the *rotational characteristic temperature* (see Chap. 6). Calculate the translational and vibrational partition functions of the molecule in the high temperature limit in the harmonic approximation, and evaluate the mean thermal energy using the expression $E = k_{\text{B}}T^2(\partial \ln Z / \partial T)_{\nu}$. Show that it leads to the same result as that obtained from the law of equipartition of energy, i.e. to $(7/2)RT$.