

# Heat capacity

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**Heat capacity** (usually denoted by a capital  $C$ , often with subscripts), or **thermal capacity**, is the measurable physical quantity that characterizes the amount of heat required to change a body's temperature by a given amount. In the International System of Units (SI), heat capacity is expressed in units of joules per kelvin.

Derived quantities that specify heat capacity as an intensive property, independent of the size of a sample, are the **molar heat capacity**, which is the heat capacity per mole of a pure substance, and the **specific heat capacity**, often simply called **specific heat**, which is the heat capacity per unit mass of a material.

Temperature reflects the average total kinetic energy of particles in matter. Heat is transfer of thermal energy; it flows from regions of high temperature to regions of low temperature. Thermal energy is stored as kinetic energy in the random modes of translation in monatomic substances, and translations and rotations of polyatomic molecules in gases. Additionally, some thermal energy may be stored as the potential energy associated with higher-energy-modes of vibration, whenever they occur in interatomic bonds in any substance. Translation, rotation, and the two types of energy in vibration (kinetic and potential) represent the degrees of freedom of motion which classically contribute to the heat capacity of a thermodynamic system.

For quantum mechanical reasons, some of these degrees of freedom may not be available, or only partially available to store thermal energy, at a given temperature. As the temperature approaches absolute zero, the specific heat capacity of a system also approaches zero, due to loss of available degrees of freedom due to the quantum mechanical effect. Quantum theory can be used to quantitatively predict specific heat capacities in simple systems.

## Background

Before the development of modern thermodynamics, it was thought that heat was a fluid, the so-called *caloric*. Bodies were capable of holding a certain amount of this fluid, hence the term *heat capacity*, named and first investigated by Joseph Black in the 1750s.<sup>[1]</sup> Today one instead discusses the internal energy of a system. This is made up of its microscopic kinetic and potential energy. Heat is no longer considered a fluid. Rather, it is a transfer of disordered energy at the microscopic level. Nevertheless, at least in English, the term "heat capacity" survives. Some other languages prefer the term **thermal capacity**, which is also sometimes used in English.

## Extensive and intensive quantities

An object's heat capacity (symbol  $C$ ) is defined as the ratio between the amount of heat energy transferred to the object and the resulting increase in temperature of the object,

$$C = \frac{Q}{\Delta T}$$

In the International System of Units, heat capacity has the unit joules per kelvin.

Heat capacity is an extensive property, meaning it is a physical property that scales with the size of a physical system. A sample containing twice the amount of substance of another requires twice the amount of heat transfer ( $Q$ ) to achieve the same change in temperature ( $\Delta T$ ).

For many experimental and theoretical purposes it is more convenient to report heat capacity as an intensive property, as an intrinsically characteristic property of a particular substance. This is most often accomplished by the specification of the property per a unit of mass. In science and engineering, such properties are often prefixed with the term *specific*.<sup>[2]</sup> International standards now recommend that specific heat capacity always refer to division by mass.<sup>[3]</sup> The units for the **specific heat capacity** are  $[c] = \frac{\text{J}}{\text{kg}\cdot\text{K}}$ .

In chemistry, the heat capacity is also often specified relative one mole, the unit for amount of substance, and is called the **molar heat capacity**, having the unit  $[C_{\text{mol}}] = \frac{\text{J}}{\text{mol}\cdot\text{K}}$ .

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For some considerations it is useful to specify the volume-specific heat capacity, commonly called volumetric heat capacity, which is the heat capacity per unit volume and has SI units  $[s] = \frac{\text{J}}{\text{m}^3 \cdot \text{K}}$ . This is used almost exclusively for liquids and solids, since for gasses it may be confused with specific heat capacity *at constant volume*.

## Metrology

The heat capacity of most systems is not a constant. Rather, it depends on the state variables of the thermodynamic system under study. In particular it is dependent on temperature itself, as well as on the pressure and the volume of the system.

Different measurements of heat capacity can therefore be performed, most commonly at constant pressure and constant volume. The values thus measured are usually subscripted (by  $p$  and  $V$ , respectively) to indicate the definition. Gases and liquids are typically also measured at constant volume. Measurements under constant pressure produce larger values than those at constant volume because the constant pressure values also include heat energy that is used to do work to expand the substance against the constant pressure as its temperature increases. This difference is particularly notable in gases where values under constant pressure are typically 30% to 66.7% greater than those at constant volume.

The specific heat capacities of substances comprising molecules (as distinct from monatomic gases) are not fixed constants and vary somewhat depending on temperature. Accordingly, the temperature at which the measurement is made is usually also specified. Examples of two common ways to cite the specific heat of a substance are as follows:

- Water (liquid):  $c_p = 4.1855 \text{ J}/(\text{g} \cdot \text{K})$  (15 °C, 101.325 kPa)
- Water (liquid):  $C_{V,H} = 74.539 \text{ J}/(\text{mol} \cdot \text{K})$  (25 °C)

For liquids and gases, it is important to know the pressure for which given heat-capacity data refer. Most published data are given for standard pressure. However, quite different standard conditions for temperature and pressure have been defined by different organizations. The International Union of Pure and Applied Chemistry (IUPAC) changed its recommendation from one Atmosphere to the round value 100 kPa ( $\approx 750.062 \text{ Torr}$ ).<sup>[4]</sup>

## Calculation

The path integral Monte Carlo method is a numerical approach for determining the values of heat capacity, based on quantum dynamical principles.

## Alternative units

An older unit of heat is the kilogram-calorie (Cal), originally defined as the energy required to raise the temperature of one kilogram of water by one degree centigrade, typically from 15°C to 16°C. The specific heat capacity of water on this scale would therefore be exactly 1 Cal/(K·kg). However, due to the temperature-dependence of the specific heat, a large number of different definitions of the calorie came into being. Whilst once it was very prevalent, especially its smaller cgs variant the gram-calorie (cal), defined so that the specific heat of water would be 1 cal/(K·g), in most fields the use of the calorie is now archaic.

In the United States other units of measure for heat capacity may be quoted in disciplines such as construction, civil engineering, and chemical engineering. A still common system is the English Engineering Units in which the mass reference is pound mass and the temperature is specified in degrees Fahrenheit or Rankine. One (rare) unit of heat is the pound calorie (lb-cal), defined as the amount of heat required to raise the temperature of one pound of water by one degree centigrade. On this scale the specific heat of water would be 1 lb-cal/(K·lb). More common is the British thermal unit, the standard unit of heat in the U.S. construction industry. This is defined such that the specific heat of water is 1 BTU/(°F·lb).

### Thermodynamic relations and definition of heat capacity

The internal energy of a closed system changes either by adding or removing heat to the system, or by the system performing work or having work done on it, written mathematically we have,

$$dU = dQ + dW$$

For work as a result of compression or expansion of the system volume we may write,

$$dU = dQ - PdV$$

If the process is performed at constant volume, then the second term of this relation vanishes and one readily obtains,

$$\left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial Q}{\partial T}\right)_V = C_V$$

This defines the *heat capacity at constant volume*,  $C_V$ .

Another useful quantity is the *heat capacity at constant pressure*,  $C_P$ . We start with the *enthalpy* of the system given by,

$$dH = dU + d(PV)$$

which from our equation for  $dU$  simplifies to,

$$dH = dQ + VdP, \text{ and therefore at constant pressure we have,}$$

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_P.$$

### Relation between heat capacities

Measuring the heat capacity, sometimes referred to as specific heat, at constant volume can be prohibitively difficult for liquids and solids. That is, small temperature changes typically require large pressures to maintain a liquid or solid at constant volume implying the containing vessel must be nearly rigid or at least very strong (see coefficient of thermal expansion and compressibility). Instead it is easier to measure the heat capacity at constant pressure (allowing the material to expand or contract as it wishes) and solve for the heat capacity at constant volume using mathematical relationships derived from the basic thermodynamic laws. Starting from the fundamental Thermodynamic Relation one can show

$$C_P - C_V = T \left(\frac{\partial p}{\partial T}\right)_{V,N} \left(\frac{\partial V}{\partial T}\right)_{p,N}$$

where the partial derivatives are taken at constant volume and constant number of particles; and constant pressure and constant number of particles, respectively.

This can also be rewritten

$$C_P - C_V = VT \frac{\alpha^2}{\beta_T}$$

where

$\alpha$  is the coefficient of thermal expansion,

$\beta_T$  is the isothermal compressibility.

The heat capacity ratio or adiabatic index is the ratio of the heat capacity at constant pressure to heat capacity at constant volume. It is sometimes also known as the isentropic expansion factor.

### Ideal gas

For an ideal gas, evaluating the partial derivatives above according to the equation of state

$$pV = nRT$$

the relation can be found to reduce to

$$C_p - C_V = nR$$

where  $n$  is number of moles of gas in the thermodynamic system under consideration, and  $R$  is the universal gas constant. Dividing through by  $n$ , this equation reduces simply to Mayer's relation,

$$C_{p,m} - C_{v,m} = R$$

where  $C_{p,m}$  and  $C_{v,m}$  are intensive property heat capacities expressed on a per mole basis at constant pressure and constant volume, respectively.

### Specific heat capacity

The specific heat capacity of a material on a per mass basis is

$$c = \frac{\partial C}{\partial m},$$

which in the absence of phase transitions is equivalent to

$$c = E_m = \frac{C}{m} = \frac{C}{\rho V},$$

where

$C$  is the heat capacity of a body made of the material in question,

$m$  is the mass of the body,

$V$  is the volume of the body, and

$\rho = \frac{m}{V}$  is the density of the material.

For gases, and also for other materials under high pressures, there is need to distinguish between different boundary conditions for the processes under consideration (since values differ significantly between different conditions). Typical processes for which a heat capacity may be defined include isobaric (constant pressure,  $dp = 0$ ) or isochoric (constant volume,  $dV = 0$ ) processes. The corresponding specific heat capacities are expressed as

$$c_p = \left( \frac{\partial C}{\partial m} \right)_p,$$

$$c_v = \left( \frac{\partial C}{\partial m} \right)_v.$$

From the results of the previous section, dividing through by the mass gives the relation

$$c_p - c_v = \frac{\alpha^2 T}{\rho \beta_T}$$

A related parameter to  $c$  is  $CV^{-1}$ , the volumetric heat capacity. In engineering practice,  $C_V$  for solids or liquids often signifies a volumetric heat capacity, rather than a constant-volume one. In such cases, the mass-specific heat capacity (specific heat) is often explicitly written with the subscript  $m$ , as  $c_m$ . Of course, from the above relationships, for solids one writes

$$c_m = \frac{C}{m} = \frac{c_{\text{volumetric}}}{\rho}.$$

For pure homogeneous chemical compounds with established molecular or molar mass or a molar quantity is established, heat capacity as an intensive property can be expressed on a per mole basis instead of a per mass basis

by the following equations analogous to the per mass equations:

$$C_{p,m} = \left( \frac{\partial C}{\partial n} \right)_p = \text{molar heat capacity at constant pressure}$$

$$C_{V,m} = \left( \frac{\partial C}{\partial n} \right)_V = \text{molar heat capacity at constant volume}$$

where  $n$  = number of moles in the body or thermodynamic system. One may refer to such a *per mole* quantity as molar heat capacity to distinguish it from specific heat capacity on a per mass basis.

### Polytropic heat capacity

The polytropic heat capacity is calculated at processes if all the thermodynamic properties (pressure, volume, temperature) change

$$C_{i,m} = \left( \frac{\partial C}{\partial n} \right) = \text{molar heat capacity at polytropic process}$$

The most important polytropic processes run between the adiabatic and the isotherm functions, the polytropic index is between **1** and the adiabatic exponent ( $\gamma$  or  $\kappa$ )

### Dimensionless heat capacity

The dimensionless heat capacity of a material is

$$C^* = \frac{C}{nR} = \frac{C}{Nk}$$

where

$C$  is the heat capacity of a body made of the material in question (J/K)

$n$  is the amount of substance in the body (mol)

$R$  is the gas constant (J/(K·mol))

$N$  is the number of molecules in the body. (dimensionless)

$k$  is Boltzmann's constant (J/(K·molecule))

In the ideal gas article, dimensionless heat capacity  $C^*$  is expressed as  $\hat{c}$ , and is related there directly to half the number of degrees of freedom per particle. This holds true for quadratic degrees of freedom, a consequence of the equipartition theorem.

More generally, the dimensionless heat capacity relates the logarithmic increase in temperature to the increase in the dimensionless entropy per particle  $S^* = S/Nk$ , measured in nats.

$$C^* = \frac{dS^*}{d \ln T}$$

Alternatively, using base 2 logarithms,  $C^*$  relates the base-2 logarithmic increase in temperature to the increase in the dimensionless entropy measured in bits.<sup>[5]</sup>

## Heat capacity at absolute zero

From the definition of entropy

$$T dS = \delta Q$$

the absolute entropy can be calculated by integrating from zero kelvins temperature to the final temperature  $T_f$

$$S(T_f) = \int_{T=0}^{T_f} \frac{\delta Q}{T} = \int_0^{T_f} \frac{\delta Q}{dT} \frac{dT}{T} = \int_0^{T_f} C(T) \frac{dT}{T}.$$

The heat capacity must be zero at zero temperature in order for the above integral not to yield an infinite absolute entropy, which would violate the third law of thermodynamics. One of the strengths of the Debye model is that (unlike the preceding Einstein model) it predicts the proper mathematical form of the approach of heat capacity toward zero, as absolute zero temperature is approached.

## Negative heat capacity (stars)

Most physical systems exhibit a positive heat capacity. However, even though it can seem paradoxical at first,<sup>[6] [7]</sup> there are some systems for which the heat capacity is *negative*. These include gravitating objects such as stars; and also sometimes some nano-scale clusters of a few tens of atoms, close to a phase transition.<sup>[8]</sup> A negative heat capacity can result in a negative temperature.

According to the virial theorem, for a self-gravitating body like a star or an interstellar gas cloud, the average potential energy  $U_{\text{Pot}}$  and the average kinetic energy  $U_{\text{Kin}}$  are locked together in the relation

$$U_{\text{Pot}} = -2U_{\text{Kin}},$$

The total energy  $U (= U_{\text{Pot}} + U_{\text{Kin}})$  therefore obeys

$$U = -U_{\text{Kin}},$$

If the system loses energy, for example by radiating energy away into space, the average kinetic energy and with it the average temperature actually *increases*. The system therefore can be said to have a negative heat capacity.<sup>[9]</sup>

A more extreme version of this occurs with black holes. According to black hole thermodynamics, the more mass and energy a black hole absorbs, the colder it becomes. On the other hand if it is a net emitter of energy, through Hawking radiation, it will become hotter and hotter until it literally boils away.

## Theory of heat capacity

### Factors that affect specific heat capacity

For any given substance, the heat capacity of a body is directly proportional to the amount of substance it contains (measured in terms of mass or moles or volume). Doubling the amount of substance in a body doubles its heat capacity, etc.

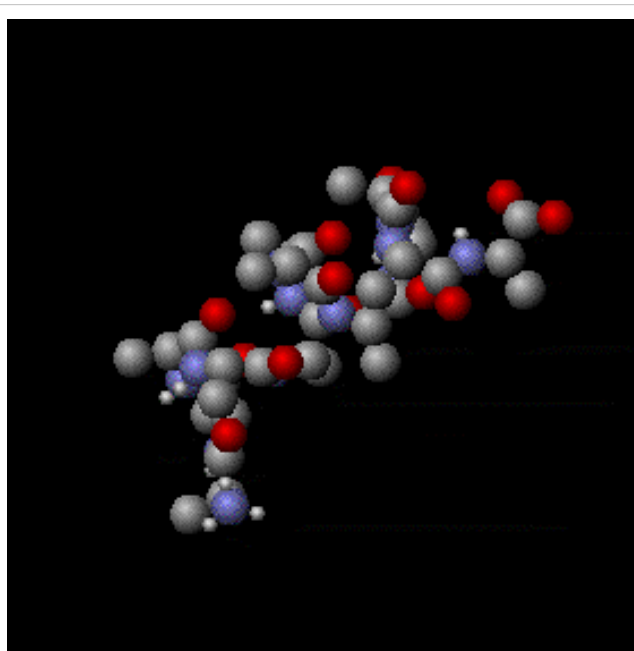
However, when this effect has been corrected for, by dividing the heat capacity by the quantity of substance in a body, the resulting specific heat capacity is a function of the structure of the substance itself. In particular, it depends on the number of degrees of freedom that are available to the particles in the substance, each of which type of freedom allows substance particles to store thermal energy. The kinetic energy of substance particles is the only one of the many possible degrees of freedom which manifests as *temperature change*, and thus the larger the number of degrees of freedom available to the particles of a substance *other* than kinetic energy, the larger will be the specific heat capacity for the substance.

In addition, quantum effects require that whenever energy be stored in any mechanism associated with a bound system which confers a degree of freedom, it must be stored in certain minimal-sized deposits (quanta) of energy, or else not stored at all. Such effects limit the full ability of some degrees of freedom to store energy when their lowest energy storage quantum amount is not easily supplied at the average energy of particles at a given temperature. In general, for this reason, specific heat capacities tend to fall at lower temperatures where the average thermal energy available to each particle degree of freedom is smaller, and thermal energy storage begins to be limited by these quantum effects. Due to this process, as temperature falls toward absolute zero, so also does heat capacity.

### Degrees of freedom

Molecules are quite different from the monatomic gases like helium and argon. With monatomic gases, thermal energy comprises only translational motions. Translational motions are ordinary, whole-body movements in 3D space whereby particles move about and exchange energy in collisions—like rubber balls in a vigorously shaken container (see animation here <sup>[12]</sup>). These simple movements in the three X, Y, and Z-axis dimensions of space means individual atoms have three translational degrees of freedom. A degree of freedom is any form of energy in which heat transferred into an object can be stored. This can be in translational kinetic energy, rotational kinetic energy, or other forms such as potential energy in vibrational modes. Only three translational degrees of freedom (corresponding to the three independent directions in space) are available for any individual atom, whether it is free, as a monatomic molecule, or bound into a polyatomic molecule.

As to rotation about an atom's axis (again, whether the atom is bound or free), its energy of rotation is proportional to the moment of inertia for the atom, which is extremely small compared to moments of inertia of collections of atoms. This is because almost all of the mass of a single atom is concentrated in its nucleus, which has a radius too small to



Molecules undergo many characteristic internal vibrations. Potential energy stored in these internal degrees of freedom contributes to a sample's energy content, <sup>[10]</sup> <sup>[11]</sup> but not its temperature. More internal degrees of freedom tend to increase a substance's specific heat capacity, so long as temperatures are high enough to overcome quantum effects.

give a significant moment of inertia. In contrast, the *spacing* of quantum energy levels for a rotating object is inversely proportional to its moment of inertia, and so this spacing becomes very large for objects with very small moments of inertia. For these reasons, the contribution from rotation of atoms on their axes is essentially zero in monatomic gases, because the energy-spacing of the associated quantum levels is too large for significant thermal energy to be stored in rotation of systems such small moments of inertia. For similar reasons, axial rotation around bonds joining atoms in diatomic gases (or along the linear axis in a linear molecule of any length) can also be neglected as a possible "degree of freedom" as well, since such rotation is similar to rotation of monatomic atoms, and so occurs about an axis with a moment of inertia too small to be able to store significant heat energy.

In polyatomic molecules, other rotational modes may become active, due to the much higher moments of inertia about certain axes which do not coincide with the linear axis of a linear molecule. These modes take the place of some translational degrees of freedom for individual atoms, since the atoms are moving in 3-D space, as the molecule rotates. The narrowing of quantum mechanically-determined energy spacing between rotational states results from situations where atoms are rotating around an axis that does not connect them, and thus form an assembly that has a large moment of inertia. This small difference between energy states allows the kinetic energy of this type of rotational motion to store heat energy at ambient temperatures. Furthermore (although usually at higher temperatures than are able to store heat in rotational motion) internal vibrational degrees of freedom also may become active (these are also a type of translation, as seen from the view of each atom). In summary, molecules are complex objects with a population of atoms that may move about within the molecule in a number of different ways (see animation at right), and each of these ways of moving is capable of storing energy if the temperature is sufficient.

The heat capacity of molecules (*on a per-atom, or atom-molar, basis*) does not exceed the heat capacity of monatomic gases, unless vibrational modes are brought into play. The reason for this is that vibrational modes allow energy to be stored as potential energy in intra-atomic bonds in a molecule, which are not available to atoms in monatomic gases. Up to about twice as much energy (on a per-atom basis) per unit of temperature increase can be stored in a solid as in a monatomic gas, by this mechanism of storing energy in the potentials of interatomic bonds. This gives many solids about twice the atom-molar heat capacity of monatomic gases, at the highest temperatures their structure can withstand.

However, quantum effects heavily affect the actual ratio at lower temperatures—especially in solids with light and tightly-bound atoms (e.g., beryllium metal). Smaller polyatomic gases store intermediate amounts of energy, giving them a *per-atom* heat capacity that is between that of monatomic gases ( $\frac{3}{2} R$  per mole, where  $R$  is the ideal gas constant), and the maximum of fully-excited warmer solids ( $3 R$  per mole). For gases, heat capacity never falls below the minimum of  $\frac{3}{2} R$  per mole, since the kinetic energy of gas molecules is always available to store this much heat energy. However, for cryogenic temperatures in solids, heat capacity falls toward zero, as temperature approaches absolute zero.

### **Example of temperature-dependent specific heat capacity, in a diatomic gas**

To illustrate the role of various degrees of freedom in storing heat, we may consider nitrogen, a diatomic molecule that has five active degrees of freedom at room temperature: the three comprising translational motion plus two rotational degrees of freedom internally. Although the constant-volume molar heat capacity of nitrogen at this temperature is five-thirds that of monatomic gases, on a per-mole of atoms basis, it is five-sixths that of a monatomic gas. The reason for this is the loss of a degree of freedom due to the bond when it does not allow storage of thermal energy. Two separate nitrogen atoms would have a total of six degrees of freedom—the three translational degrees of freedom of each atom. When the atoms are bonded the molecule will still only have three translational degrees of freedom, as the two atoms in the molecule move as one. However, the molecule cannot be treated as a point object, and the moment of inertia has increased sufficiently about two axes to allow two rotational degrees of freedom to be active at room temperature to give five degrees of freedom. The moment of inertia about the third axis remains small, as this is the axis passing through the centres of the two atoms, and so is similar to the small moment of inertia



for atoms of a monatomic gas. Thus, this degree of freedom does not act to store heat, and does not contribute to the heat capacity of nitrogen. The heat capacity *per atom* for nitrogen is therefore less than for a monatomic gas, so long as the temperature remains low enough that no vibrational degrees of freedom are activated.<sup>[13]</sup>

At higher temperatures, however, nitrogen gas gains two more degrees of internal freedom, as the molecule is excited into higher vibrational modes which store thermal energy. Now the bond is contributing heat capacity, and is contributing more than if the atoms were not bonded. With full thermal excitation of bond vibration, the heat capacity per volume or mole of molecules approaches seven-thirds that of monatomic gases, or seven-sixths of monatomic, on a mole-of-atoms basis. This is now a *higher* heat capacity per atom than the monatomic figure, because the vibrational mode enables an extra degree of *potential energy* freedom per pair of atoms, which monatomic gases cannot possess.<sup>[14]</sup> See thermodynamic temperature for more information on translational motions, kinetic (heat) energy, and their relationship to temperature.

However, even at these large temperatures where gaseous nitrogen stores  $7/6$ <sup>th</sup> of the energy *per atom* of a monatomic gas (making it more efficient at storing energy on an atomic basis), it still only stores  $7/12$ <sup>th</sup> of the maximal per-atom heat capacity of a solid, meaning it is not as efficient on an atomic basis, as substances can be. This is because many of the potential bonds which might be storing potential energy in gaseous nitrogen (as opposed to solid nitrogen) are lacking, because only one of the spacial dimensions for each nitrogen atom offers a bond into which potential energy can be stored, without increasing the kinetic energy of the atom. In general, solids are most efficient, on an atomic basis, at storing thermal energy (that is, they have the highest per-atom or per-mole-of-atoms heat capacity).

### **Per mole of...**

#### **Per mole of molecules**

When the specific heat capacity,  $c$ , of a material is measured (lowercase  $c$  means the unit quantity is in terms of mass), different values arise because different substances have different molar masses (essentially, the weight of the individual atoms or molecules). In solids, thermal energy arises due to the number of atoms that are vibrating. "Molar" heat capacity *per mole of molecules*, for both gases and solids, offer figures which are arbitrarily large, since molecules may be arbitrarily large. Such heat capacities are thus not intensive quantities for this reason, since the quantity of mass being considered can be increased without limit.

#### **Per mole of atoms**

Conversely, for *molecular-based* substances (which also absorb heat into their internal degrees of freedom), massive, complex molecules with high atomic count—like octane—can store a great deal of energy per mole and yet are quite unremarkable on a mass basis, or on a per-atom basis. This is because, in fully excited systems, heat is stored independently by each atom in a substance, not primarily by the bulk motion of molecules.

Thus, it is the heat capacity per-mole-of-atoms, not per-mole-of-molecules, which is the intensive quantity, and which comes closest to being a constant for all substances at high temperatures. This relationship was noticed empirically in 1819, and is called the Dulong-Petit law, after its two discoverers.<sup>[15]</sup> Historically, the fact that specific heat capacities are approximately equal when corrected by the presumed weight of the atoms of solids, was an important piece of data in favor of the atomic theory of matter.

Because of the connection of heat capacity to the number of atoms, some care should be taken to specify a mole-of-molecules basis vs. a mole-of-atoms basis, when comparing specific heat capacities of molecular solids and gases. Ideal gases have the same numbers of molecules per volume, so increasing molecular complexity adds heat capacity on a per-volume and per-mole-of-molecules basis, but may lower or raise heat capacity on a per-atom basis, depending on whether the temperature is sufficient to store energy as atomic vibration.

In solids, the quantitative limit of heat capacity in general is about  $3R$  per mole of atoms, where  $R$  is the ideal gas constant. This  $3R$  value is about  $24.9 \text{ J/mole.K}$ . Six degrees of freedom (three kinetic and three potential) are

available to each atom. Each of these six contributes  $\frac{1}{2}R$  specific heat capacity per mole of atoms.<sup>[16]</sup> This limit of  $3R$  per mole specific heat capacity is approached at room temperature for most solids, with significant departures at this temperature only for solids composed of the lightest atoms which are bound very strongly, such as beryllium (where the value is only of 66% of  $3R$ ), or diamond (where it is only 24% of  $3R$ ). These large departures are due to quantum effects which prevent full distribution of heat into all vibrational modes, when the energy difference between vibrational quantum states is very large compared to the average energy available to each atom from the ambient temperature.

For monatomic gases, the specific heat is only half of  $3R$  per mole, i.e. ( $\frac{3}{2}R$  per mole) due to loss of all potential energy degrees of freedom in these gases. For polyatomic gases, the heat capacity will be intermediate between these values on a per-mole-of-atoms basis, and (for heat-stable molecules) would approach the limit of  $3R$  per mole of atoms, for gases composed of complex molecules, and at higher temperatures at which all vibrational modes accept excitational energy. This is because very large and complex gas molecules may be thought of as relatively large blocks of solid matter which have lost only a relatively small fraction of degrees of freedom, as compared to a fully-integrated solid.

### **Corollaries of these considerations for solids (volume-specific heat capacity)**

Since the bulk density of a solid chemical element is strongly related to its molar mass (usually about  $3R$  per mole, as noted above), there exists noticeable inverse correlation between a solid's density and its specific heat capacity on a per-mass basis. This is due to a very approximate tendency of atoms of most elements to be about the same size, despite much wider variations in density and atomic weight. These two factors (constancy of atomic volume and constancy of mole-specific heat capacity) result in a good correlation between the *volume* of any given solid chemical element and its total heat capacity. Another way of stating this, is that the volume-specific heat capacity (volumetric heat capacity) of solid elements is roughly a constant. The molar volume of solid elements is very roughly constant, and (even more reliably) so also is the molar heat capacity for most solid substances. These two factors determine the volumetric heat capacity, which as a bulk property may be striking in consistency. For example, the element uranium is a metal which has a density almost 36 times that of the metal lithium, but uranium's specific heat capacity on a volumetric basis (i.e. per given volume of metal) is only 18% larger than lithium's.

Since the volume-specific corollary of the Dulong-Petit specific heat capacity relationship requires that atoms of all elements take up (on average) the same volume in solids, there are many departures from it, with most of these due to variations in atomic size. For instance, arsenic, which is only 14.5% less dense than antimony, has nearly 59% more specific heat capacity on a mass basis. In other words; even though an ingot of arsenic is only about 17% larger than an antimony one of the same mass, it absorbs about 59% more heat for a given temperature rise. The heat capacity ratios of the two substances closely follows the ratios of their molar volumes (the ratios of numbers of atoms in the same volume of each substance); the departure from the correlation to simple volumes in this case is due to lighter arsenic atoms being significantly more closely-packed than antimony atoms, instead of similar size. In other words, similar-sized atoms would cause a mole of arsenic to be 63% larger than a mole of antimony, with a correspondingly lower density, allowing its volume to more closely mirror its heat capacity behavior.

## Other factors

### Hydrogen bonds

Hydrogen-containing polar molecules like ethanol, ammonia, and water have powerful, intermolecular hydrogen bonds when in their liquid phase. These bonds provide another place where heat may be stored as potential energy of vibration, even at comparatively low temperatures. Hydrogen bonds account for the fact that liquid water stores nearly the theoretical limit of  $3R$  per mole of atoms, even at relatively low temperatures (i.e. near the freezing point of water).

### Impurities

In the case of alloys, there are several conditions in which small impurity concentrations can greatly affect the specific heat. Alloys may exhibit marked difference in behaviour even in the case of small amounts of impurities being one element of the alloy; for example impurities in semiconducting ferromagnetic alloys may lead to quite different specific heat properties.<sup>[17]</sup>

## The simple case of the monatomic gas

In the case of a monatomic gas such as helium under constant volume, if it is assumed that no electronic or nuclear quantum excitations occur, each atom in the gas has only 3 degrees of freedom, all of a translational type. No energy dependence is associated with the degrees of freedom which define the position of the atoms. While, in fact, the degrees of freedom corresponding to the momenta of the atoms are quadratic, and thus contribute to the heat capacity. There are  $N$  atoms, each of which has 3 components of momentum, which leads to  $3N$  total degrees of freedom. This gives:

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{3}{2} N k_B = \frac{3}{2} n R$$

$$C_{V,m} = \frac{C_V}{n} = \frac{3}{2} R$$

where

$C_V$  is the heat capacity at constant volume of the gas

$C_{V,m}$  is the *molar heat capacity* at constant volume of the gas

$N$  is the total number of atoms present in the container

$n$  is the number of moles of atoms present in the container ( $n$  is the ratio of  $N$  and Avogadro's number)

$R$  is the ideal gas constant, (8.314570[70] J/(mol·K)).  $R$  is equal to the product of Boltzmann's constant  $k_B$  and Avogadro's number

The following table shows experimental molar constant volume heat capacity measurements taken for each noble monatomic gas (at 1 atm and 25 °C):

Monatomic gas	$C_{V,m}$ (J/(mol·K))	$C_{V,m}/R$
He	12.5	1.50
Ne	12.5	1.50
Ar	12.5	1.50
Kr	12.5	1.50
Xe	12.5	1.50

It is apparent from the table that the experimental heat capacities of the monatomic noble gases agrees with this simple application of statistical mechanics to a very high degree.

The molar heat capacity of a monatomic gas at constant pressure is then

$$C_{p,m} = C_{V,m} + R = \frac{5}{2}R$$

### Diatomic gas

In the somewhat more complex case of an ideal gas of diatomic molecules, the presence of internal degrees of freedom are apparent. In addition to the three translational degrees of freedom, there are rotational and vibrational degrees of freedom. In general, the number of degrees of freedom,  $f$ , in a molecule with  $n_a$  atoms is  $3n_a$ :

$$f = 3n_a$$

Mathematically, there are a total of three rotational degrees of freedom, one corresponding to rotation about each of the axes of three dimensional space. However, in practice only the existence of two degrees of rotational freedom for linear molecules will be considered. This approximation is valid because the moment of inertia about the internuclear axis is vanishingly small with respect other moments of inertia in the molecule (this is due to the extremely small radii of the atomic nuclei, compared to the distance between them in a molecule). Quantum mechanically, it can be shown that the interval between successive rotational energy eigenstates is inversely proportional to the moment of inertia about that axis. Because the moment of inertia about the internuclear axis is vanishingly small relative to the other two rotational axes, the energy spacing can be considered so high that no excitations of the rotational state can possibly occur unless the temperature is extremely high. It is easy to calculate the expected number of vibrational degrees of freedom (or vibrational modes). There are three degrees of translational freedom, and two degrees of rotational freedom, therefore

$$f_{\text{vib}} = f - f_{\text{trans}} - f_{\text{rot}} = 6 - 3 - 2 = 1$$

Each rotational and translational degree of freedom will contribute  $R/2$  in the total molar heat capacity of the gas. Each vibrational mode will contribute  $R$  to the total molar heat capacity, however. This is because for each vibrational mode, there is a potential and kinetic energy component. Both the potential and kinetic components will contribute  $R/2$  to the total molar heat capacity of the gas. Therefore, a diatomic molecule would be expected to have a molar constant-volume heat capacity of

$$C_{V,m} = \frac{3R}{2} + R + R = \frac{7R}{2} = 3.5R$$

where the terms originate from the translational, rotational, and vibrational degrees of freedom, respectively.

The following is a table of some molar constant-volume heat capacities of various diatomic gases at standard temperature ( $25^\circ\text{C} = 298\text{ K}$ )

Diatomic gas	$C_{V,m}$ (J/(mol·K))	$C_{V,m} / R$
H <sub>2</sub>	20.18	2.427
CO	20.2	2.43
N <sub>2</sub>	19.9	2.39
Cl <sub>2</sub>	24.1	3.06
Br <sub>2</sub> (vapour)	28.2	3.39

From the above table, clearly there is a problem with the above theory. All of the diatomics examined have heat capacities that are lower than those predicted by the equipartition theorem, except Br<sub>2</sub>. However, as the atoms composing the molecules become heavier, the heat capacities move closer to their expected values. One of the reasons for this phenomenon is the quantization of vibrational, and to a lesser extent, rotational states. In fact, if it is assumed that the molecules remain in their lowest energy vibrational state because the inter-level energy spacings for vibration-energies are large, the predicted molar constant volume heat capacity for a diatomic molecule becomes just that from the contributions of translation and rotation:

$$C_{V,m} = \frac{3R}{2} + R = \frac{5R}{2} = 2.5R$$

which is a fairly close approximation of the heat capacities of the lighter molecules in the above table. If the quantum harmonic oscillator approximation is made, it turns out that the quantum vibrational energy level spacings are actually inversely proportional to the square root of the reduced mass of the atoms composing the diatomic molecule. Therefore, in the case of the heavier diatomic molecules such as chlorine or bromine, the quantum vibrational energy level spacings become finer, which allows more excitations into higher vibrational levels at lower temperatures. This limit for storing heat capacity in vibrational modes, as discussed above, becomes  $7R/2 = 3.5R$  per mole, which is fairly consistent with the measured value for Br<sub>2</sub> at room temperature. As temperatures rise, all diatomic gases approach this value.

## General gas phase

The specific heat of the gas is best conceptualized in terms of the degrees of freedom of an individual molecule. The different degrees of freedom correspond to the different ways in which the molecule may store energy. The molecule may store energy in its translational motion according to the formula:

$$E = \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2)$$

where  $m$  is the mass of the molecule and  $[v_x, v_y, v_z]$  is velocity of the center of mass of the molecule. Each direction of motion constitutes a degree of freedom, so that there are three translational degrees of freedom.

In addition, a molecule may have rotational motion. The kinetic energy of rotational motion is generally expressed as

$$E = \frac{1}{2} (I_1\omega_1^2 + I_2\omega_2^2 + I_3\omega_3^2)$$

where  $I$  is the moment of inertia tensor of the molecule, and  $[\omega_1, \omega_2, \omega_3]$  is the angular velocity pseudo-vector (in a coordinate system aligned with the principle axes of the molecule). In general, then, there will be three additional degrees of freedom corresponding to the rotational motion of the molecule, (For linear molecules one of the inertia tensor terms vanishes and there are only two rotational degrees of freedom). The degrees of freedom corresponding to translations and rotations are called the rigid degrees of freedom, since they do not involve any deformation of the molecule.

The motions of the atoms in a molecule which are not part of its gross translational motion or rotation may be classified as vibrational motions. It can be shown that if there are  $n$  atoms in the molecule, there will be as many as  $v = 3n - 3 - n_r$  vibrational degrees of freedom, where  $n_r$  is the number of rotational degrees of freedom. A

vibrational degree of freedom corresponds to a specific way in which all the atoms of a molecule can vibrate. The actual number of possible vibrations may be less than this maximal one, due to various symmetries.

For example, triatomic nitrous oxide  $\text{N}_2\text{O}$  will have only 2 degrees of rotational freedom (since it is a linear molecule) and contains  $n=3$  atoms: thus the number of possible vibrational degrees of freedom will be  $v = (3 \cdot 3) - 3 - 2 = 4$ . There are four ways or "modes" in which the three atoms can vibrate, corresponding to 1) A mode in which an atom at each end of the molecule moves away from, or towards, the center atom at the same time, 2) a mode in which either end atom moves asynchronously with regard to the other two, and 3) and 4) two modes in which the molecule bends out of line, from the center, in the two possible planar directions that are orthogonal to its axis. Each vibrational degree of freedom confers TWO total degrees of freedom, since vibrational energy mode partitions into 1 kinetic and 1 potential mode. This would give nitrous oxide 3 translational, 2 rotational, and 4 vibrational modes (but these last giving 8 vibrational degrees of freedom), for storing energy. This is a total of  $f = 3+2+8 = 13$  total energy-storing degrees of freedom, for  $\text{N}_2\text{O}$ .

For a bent molecule like water  $\text{H}_2\text{O}$ , a similar calculation gives  $9-3-3 = 3$  modes of vibration, and 3 (translational) + 3 (rotational) + 6(vibrational) = 12 degrees of freedom.

### The storage of energy into degrees of freedom

If the molecule could be entirely described using classical mechanics, then the theorem of equipartition of energy could be used to predict that each degree of freedom would have an average energy in the amount of  $(1/2)kT$  where  $k$  is Boltzmann's constant and  $T$  is the temperature. Our calculation of the constant-volume heat capacity would be straightforward. Each molecule would be holding, on average, an energy of  $(f/2)kT$  where  $f$  is the total number of degrees of freedom in the molecule. Note that  $Nk = R$  if  $N$  is Avogadro's number, which is the case in considering the heat capacity of a mole of molecules. Thus, the total internal energy of the gas would be  $(f/2)NkT$  where  $N$  is the total number of molecules. The heat capacity (at constant volume) would then be a constant  $(f/2)Nk$  the mole-specific heat capacity would be  $(f/2)R$  the molecule-specific heat capacity would be  $(f/2)k$  and the dimensionless heat capacity would be just  $f/2$ . Here again, each vibrational degree of freedom contributes  $2f$ . Thus, a mole of nitrous oxide would have a total constant-volume heat capacity (including vibration) of  $(13/2)R$  by this calculation.

In summary, the molar heat capacity (mole-specific heat capacity) of an ideal gas with  $f$  degrees of freedom is given by

$$C_{V,m} = \frac{f}{2}R$$

This equation applies to all polyatomic gases, if the degrees of freedom are known.<sup>[18]</sup>

The constant-pressure heat capacity for any gas would exceed this by an extra factor of  $R$  (see Mayer's relation, above). As example  $C_p$  would be a total of  $(15/2)R$ /mole for nitrous oxide.

### The effect of quantum energy levels in storing energy in degrees of freedom

The various degrees of freedom cannot generally be considered to obey classical mechanics, however. Classically, the energy residing in each degree of freedom is assumed to be continuous—it can take on any positive value, depending on the temperature. In reality, the amount of energy that may reside in a particular degree of freedom is quantized: It may only be increased and decreased in finite amounts. A good estimate of the size of this minimum amount is the energy of the first excited state of that degree of freedom above its ground state. For example, the first vibrational state of the hydrogen chloride (HCl) molecule has an energy of about  $5.74 \times 10^{-20}$  joule. If this amount of energy were deposited in a classical degree of freedom, it would correspond to a temperature of about 4156 K.

If the temperature of the substance is so low that the equipartition energy of  $(1/2)kT$  is much smaller than this excitation energy, then there will be little or no energy in this degree of freedom. This degree of freedom is then said to be "frozen out". As mentioned above, the temperature corresponding to the first excited vibrational state of HCl is

about 4156 K. For temperatures well below this value, the vibrational degrees of freedom of the HCl molecule will be frozen out. They will contain little energy and will not contribute to the thermal energy or the heat capacity of HCl gas.

### Energy storage mode "freeze-out" temperatures

It can be seen that for each degree of freedom there is a critical temperature at which the degree of freedom "unfreezes" and begins to accept energy in a classical way. In the case of translational degrees of freedom, this temperature is that temperature at which the thermal wavelength of the molecules is roughly equal to the size of the container. For a container of macroscopic size (e.g. 10 cm) this temperature is extremely small and has no significance, since the gas will certainly liquify or freeze before this low temperature is reached. For any real gas translational degrees of freedom may be considered to always be classical and contain an average energy of  $(3/2)kT$  per molecule.

The rotational degrees of freedom are the next to "unfreeze". In a diatomic gas, for example, the critical temperature for this transition is usually a few tens of kelvins, although with a very light molecule such as hydrogen the rotational energy levels will be spaced so widely that rotational heat capacity may not completely "unfreeze" until considerably higher temperatures are reached. Finally, the vibrational degrees of freedom are generally the last to unfreeze. As an example, for diatomic gases, the critical temperature for the vibrational motion is usually a few thousands of kelvins, and thus for the nitrogen in our example at room temperature, no vibration modes would be excited, and the constant-volume heat capacity at room temperature is  $(5/2)R/\text{mole}$ , not  $(7/2)R/\text{mole}$ . As seen above, with some unusually heavy gases such as iodine gas  $\text{Cl}_2$ , or bromine gas  $\text{Br}_2$ , some vibrational heat capacity may be observed even at room temperatures.

It should be noted that it has been assumed that atoms have no rotational or internal degrees of freedom. This is in fact untrue. For example, atomic electrons can exist in excited states and even the atomic nucleus can have excited states as well. Each of these internal degrees of freedom are assumed to be frozen out due to their relatively high excitation energy. Nevertheless, for sufficiently high temperatures, these degrees of freedom cannot be ignored. In a few exceptional cases, such molecular electronic transitions are of sufficiently low energy that they contribute to heat capacity at room temperature, or even at cryogenic temperatures. One example of an electronic transition degree of freedom which contributes heat capacity at standard temperature is that of nitric oxide (NO), in which the single electron in an anti-bonding molecular orbital has energy transitions which contribute to the heat capacity of the gas even at room temperature.

An example of a nuclear magnetic transition degree of freedom which is of importance to heat capacity, is the transition which converts the spin isomers of hydrogen gas ( $\text{H}_2$ ) into each other. At room temperature, the proton spins of hydrogen gas are aligned 75% of the time, resulting in *orthohydrogen* when they are. Thus, some thermal energy has been stored in the degree of freedom available when *parahydrogen* (in which spins are anti-aligned) absorbs energy, and is converted to the higher energy ortho form. However, at the temperature of liquid hydrogen, not enough heat energy is available to produce orthohydrogen (that is, the transition energy between forms is large enough to "freeze out" at this low temperature), and thus the parahydrogen form predominates. The heat capacity of the transition is sufficient to release enough heat, as orthohydrogen converts to the lower-energy parahydrogen, to boil the hydrogen liquid to gas again, if this evolved heat is not removed with a catalyst after the gas has been cooled and condensed. This example also illustrates the fact that some modes of storage of heat may not be in constant equilibrium with each other in substances, and heat absorbed or released from such phase changes may "catch up" with temperature changes of substances, only after a certain time. In other words, the heat evolved and absorbed from the ortho-para isomeric transition contributes to the heat capacity of hydrogen on long time-scales, but not on *short* time-scales. These time scales may also depend on the presence of a catalyst.

Less exotic phase-changes may contribute to the heat-capacity of substances and systems, as well, as (for example) when water is converted back and forth from solid to liquid or gas form. Phase changes store heat energy entirely in

breaking the bonds of the potential energy interactions between molecules of a substance. As in the case of hydrogen, it is also possible for phase changes to be hindered as the temperature drops, so that they do not catch up and become apparent, without a catalyst. For example, it is possible to supercool liquid water to below the freezing point, and not observe the heat evolved when the water changes to ice, so long as the water remains liquid. This heat appears instantly when the water freezes.

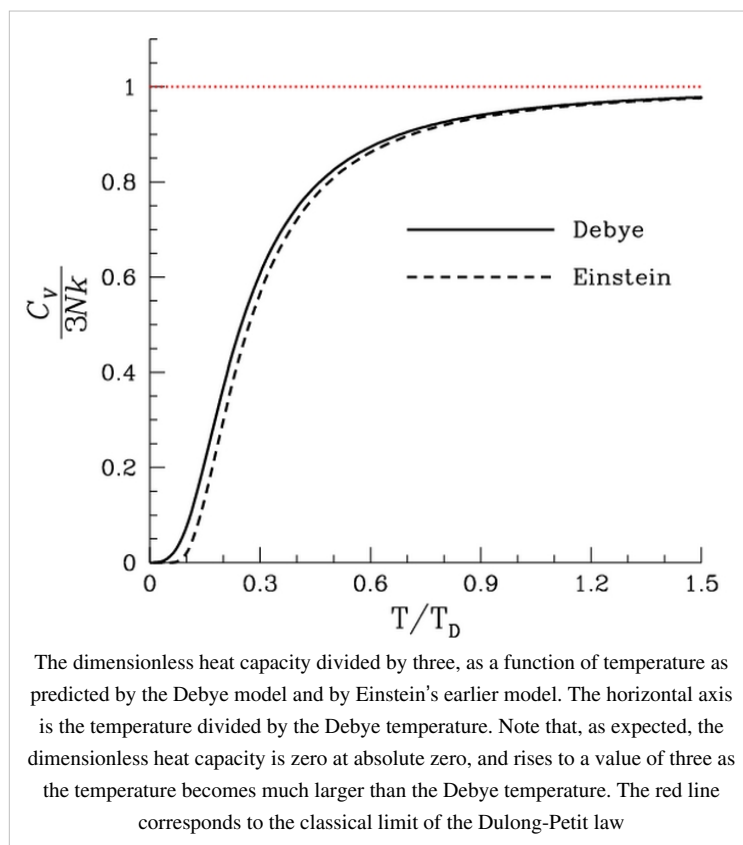
## Solid phase

For matter in a crystalline solid phase, the Dulong-Petit law, which was discovered empirically, states that the mole-specific heat capacity assumes the value  $3R$ . Indeed, for solid metallic chemical elements at room temperature, molar heat capacities range from about  $2.8R$  to  $3.4R$ . Large exceptions involve solids composed of light, tightly-bonded atoms such as beryllium at  $2.0R$ , and diamond at only  $0.735R$ . The latter conditions create large quantum vibrational energy spacing, so that many vibrational modes are not available (are frozen out) at room temperature.

The theoretical maximum heat capacity for larger and larger multi-atomic gases at higher temperatures, also approaches the Dulong-Petit limit of  $3R$ , so long as this is calculated per mole of atoms, not molecules. The reason is that gases with very large molecules, in theory have almost the same high-temperature heat capacity as solids, lacking only the (small) heat capacity contribution that comes from potential energy that cannot be stored between separate molecules in a gas.

The Dulong-Petit limit results from the equipartition theorem, and as such is only valid in the classical limit of a microstate continuum, which is a high temperature limit. For light and non-metallic elements, as well as most of the common molecular solids based on carbon compounds at standard ambient temperature, quantum effects may also play an important role, as they do in multi-atomic gases. These effects usually combine to give heat capacities lower than  $3R$  per mole of *atoms* in the solid, although in molecular solids, heat capacities calculated *per mole of molecules* in molecular solids may be more than  $3R$ . For example, the heat capacity of water ice at the melting point is about  $4.6R$  per mole of molecules, but only  $1.5R$  per mole of atoms. The lower than  $3R$  number "per atom" (as is the case with diamond and beryllium) results from the "freezing out" of possible vibration modes for light atoms at suitably low temperatures, just as in many low-mass-atom gases at room temperatures. Because of high crystal binding energies, these effects are seen in solids more often than liquids: for example the heat capacity of liquid water is twice that of ice at near the same temperature, and is again close to the  $3R$  per mole of atoms of the Dulong-Petit theoretical maximum.

For a more modern and precise analysis of the heat capacities of solids, especially at low temperatures, it is useful to use the idea of phonons. See Debye model.





The specific heat of amorphous materials has characteristic discontinuities at the glass transition temperature due to rearrangements that occur in the distribution of atoms.<sup>[19]</sup> These discontinuities are frequently used to detect the glass transition temperature where a supercooled liquid transforms to a glass.<sup>[20]</sup>

## Table of specific heat capacities

Note that especially high values, as for paraffin, water and ammonia, result from calculating specific heats in terms of moles of molecules. If specific heat is expressed per mole of atoms for these substances, few constant-volume values exceed the theoretical Dulong-Petit limit of  $25 \text{ J}/(\text{mol}\cdot\text{K}) = 3 R$  per mole of atoms.

**Table of specific heat capacities at 25 °C unless otherwise noted**

Substance	Phase	$c_p$ $\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$	$C_{p,m}$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$C_{v,m}$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	Volumetric heat capacity $\text{J}\cdot\text{cm}^{-3}\cdot\text{K}^{-1}$
Air (Sea level, dry, 0 °C)	gas	1.0035	29.07	20.7643	0.001297
Air (typical room conditions <sup>A</sup> )	gas	1.012	29.19	20.85	
Aluminium	solid	0.897	24.2		2.422
Ammonia	liquid	4.700	<b>80.08</b>		3.263
Animal (and human) tissue <sup>[21]</sup>	mixed	3.5	—		3.7*
Antimony	solid	0.207	25.2		1.386
Argon	gas	0.5203	20.7862	12.4717	
Arsenic	solid	0.328	24.6		1.878
Beryllium	solid	1.82	16.4		3.367
Bismuth <sup>[22]</sup>	solid	0.123	25.7		1.20
Cadmium	solid	0.231	—		—
Carbon dioxide CO <sub>2</sub> <sup>[18]</sup>	gas	0.839*	36.94	28.46	
Chromium	solid	0.449	—		—
Copper	solid	0.385	24.47		3.45
Diamond	solid	0.5091	<b>6.115</b>		1.782
Ethanol	liquid	2.44	112		1.925
Gasoline	liquid	2.22	228		1.64
Glass <sup>[22]</sup>	solid	0.84			
Gold	solid	0.129	25.42		2.492
Granite <sup>[22]</sup>	solid	0.790			2.17
Graphite	solid	0.710	8.53		1.534
Helium	gas	5.1932	20.7862	12.4717	
Hydrogen	gas	<b>14.30</b>	28.82		
Hydrogen sulfide H <sub>2</sub> S <sup>[18]</sup>	gas	1.015*	34.60		
Iron	solid	0.450	25.1		3.537

Lead	solid	0.129	26.4		1.44
Lithium	solid	3.58	24.8		1.912
Lithium at 181 °C <sup>[23]</sup>	liquid	<b>4.379</b>	30.33		2.242
Magnesium	solid	1.02	24.9		1.773
Mercury	liquid	0.1395	27.98		1.888
Methane at 2 °C	gas	2.191			
Methanol	liquid	2.597	—		—
Nitrogen	gas	1.040	29.12	20.8	
Neon	gas	1.0301	20.7862	12.4717	
Oxygen	gas	0.918	29.38		
Paraffin wax	solid	2.5	<b>900</b>		2.325
Polyethylene (rotomolding grade) <sup>[24]</sup>	solid	2.3027			
Polyethylene (rotomolding grade) <sup>[24]</sup>	liquid	2.9308			
Silica (fused)	solid	0.703	42.2		1.547
Silver <sup>[22]</sup>	solid	0.233	24.9		2.44
Sodium	solid	1.230	—		—
Tin	solid	0.227	—		—
Titanium	solid	0.523	—		—
Tungsten <sup>[22]</sup>	solid	0.134	24.8		2.58
Uranium	solid	<b>0.116</b>	27.7		2.216
Water at 100 °C (steam)	gas	<b>2.080</b>	<b>37.47</b>	<b>28.03</b>	
Water at 25 °C	liquid	<b>4.1813</b>	<b>75.327</b>	<b>74.53</b>	<b>4.1796</b>
Water at 100 °C	liquid	<b>4.1813</b>	<b>75.327</b>	<b>74.53</b>	<b>4.2160</b>
Water at −10 °C (ice) <sup>[22]</sup>	solid	<b>2.11</b>	<b>38.09</b>		<b>1.938</b>
Zinc <sup>[22]</sup>	solid	0.387	25.2		2.76
<b>Substance</b>	<b>Phase</b>	<b><math>C_p</math> J/(g·K)</b>	<b><math>C_{p,m}</math> J/(mol·K)</b>	<b><math>C_{v,m}</math> J/(mol·K)</b>	<b>Volumetric heat capacity J/(cm<sup>3</sup>·K)</b>

<sup>A</sup> Assuming an altitude of 194 metres above mean sea level (the world-wide median altitude of human habitation), an indoor temperature of 23 °C, a dewpoint of 9 °C (40.85% relative humidity), and 760 mm-Hg sea level-corrected barometric pressure (molar water vapor content = 1.16%).

\*Derived data by calculation. This is for water-rich tissues such as brain. The whole-body average figure for mammals is approximately 2.9 J/(cm<sup>3</sup>·K) <sup>[25]</sup>

## Specific heat capacity of building materials

(Usually of interest to builders and solar designers)

### Specific heat capacity of building materials

Substance	Phase	$c_p$ J/(g·K)
Asphalt	solid	0.920
Brick	solid	0.840
Concrete	solid	0.880
Glass, silica	solid	0.840
Glass, crown	solid	0.670
Glass, flint	solid	0.503
Glass, pyrex	solid	0.753
Granite	solid	0.790
Gypsum	solid	1.090
Marble, mica	solid	0.880
Sand	solid	0.835
Soil	solid	0.800
Wood	solid	1.7 (1.2 to 2.3)
Substance	Phase	$c_p$ J/(g·K)

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