

A note on the variation of specific heats in ideal gases

Most diatomic gases such as nitrogen (N₂) and oxygen (O₂) at or near room temperature have specific heats (c_v and c_p) that are almost constant. However, as the temperature (T) rises above about 700 K, the specific heat begins to rise. Because the relation

$$c_p(T) - c_v(T) = R$$

remains valid, where R is the gas constant, it is sufficient to discuss (and calculate) the variation of one of the specific heats with T . We shall talk about c_v in this note.

In the following discussion all energies are mass specific, i.e. expressed per unit mass, and denoted by lower case quantities. Energies per mole are obtained by multiplying mass specific by the molar mass. In equations that contain the particular gas constant R , the molar energy is obtained by substituting the universal gas constant \hat{R} for R .

Recall that "specific heat" is a somewhat misleading term that dates back to the time when heat was viewed as a fluid that could be held by a material, hence terms like specific heat, heat capacity, etc. Today we know that "heat" and "work" should always be understood as "heat transfer" and "work transfer" because each is an energy transfer. Heat transfer is energy transfer with entropy transfer; work transfer is energy transfer without entropy transfer. This is the only way one can distinguish reliably between heat and work transfers.

The precise technical definitions of specific heat are

$$c_v \equiv \left(\frac{\partial u}{\partial T} \right)_v ; c_p \equiv \left(\frac{\partial h}{\partial T} \right)_p .$$

c_v measures the rate of change of internal energy, u , with T . The internal energy u of any substance is the energy stored in the molecules. In an ideal gas, the molecules are far apart on the average, and the internal energy depends only on the energy stored in individual molecules, and not on the separation between molecules. More precisely, the molecules are usually so far apart, and spend so little time close to each other when they do collide, that the potential energy associated with changing their average separation is negligible. If the energy did depend on the average separation of molecules (i.e. the density), as it does in liquids and gases, then $u = u(T, \rho)$, whereas in an ideal gas $u \neq u(\rho)$. Thus, for ideal gases the partial derivatives above, become ordinary derivatives:

$$c_v = \frac{du}{dT} ; c_p = \frac{dh}{dT} .$$

For an ideal gas the internal energy is the sum of the kinetic energy of motion of the center of mass of each individual molecule and the energy of motion relative to this center of mass. Even if the bulk gas is at rest, the (centers of mass of) individual molecules are in constant chaotic motion - that is sometimes referred to as the thermal energy. In fact, in non-equilibrium situations, the temperature is often *defined* by the average kinetic energy of random motion of the molecules, e_{tr} .

$$e_{tr} = 3 \left(\frac{1}{2} RT \right) = \frac{3}{2} RT$$

For most diatomic molecules the rotation of the nuclei give the molecules an average rotational energy e_{rot} that is given by

$$e_{rot} = 2 \left(\frac{1}{2} RT \right) = RT .$$

(Hydrogen gas at low temperatures is an exception important in propulsion systems.) If we assume that the internal energy is the sum of these two contributions

$$u = e_{tr} + e_{rot} = \frac{3}{2} RT + RT = \frac{5}{2} RT .$$

Then

$$c_v = \frac{du}{dT} = \frac{5}{2} R; \quad c_p = c_v + R = \frac{7}{2} R; \quad \gamma = \frac{c_p}{c_v} = \frac{7}{5} = 1.4$$

These results were first known from experiment, and were then explained by classical statistical mechanics which predicted that at equilibrium each "degree of freedom" would contribute $\frac{1}{2}RT$ to the internal energy. Thus translation has three degrees of freedom because the molecule can move in 3-dimensional space, and a diatomic molecule has two additional degrees of freedom because it can rotate about two orthogonal axes. (There is only a very small moment of inertia about the internuclear axis, so no energy can be stored in rotation about this axis.) In this model the nuclei are assumed to be effectively connected by a rigid massless rod, so the molecule looked like a tiny dumbbell.

However, classical statistical mechanics could not deal with the observed increase in specific heat at high temperature. If it was assumed that the nuclei were not rigidly connected but could vibrate, then one would have to admit two additional degrees of freedom to the system (potential and kinetic energy of the oscillation) at all temperatures (not just high temperatures). In the classical model

$$\begin{aligned} e_{vib \text{ classical}} &= 2 \times \frac{1}{2} RT = RT; \\ u_{\text{classical}} &= e_{tr} + e_{rot} + e_{vib \text{ classical}} = \frac{7}{2} RT; \\ c_{v,\text{classical}} &= \frac{7}{2} R; \quad c_{p,\text{classical}} = \frac{9}{2} R; \quad \gamma_{\text{classical}} = \frac{9}{7} \text{ at all } T! \end{aligned}$$

Unfortunately, none of these predictions is in agreement with experiment, and the discovery that there were free electrons in atoms made the situation worse, because now the energy of the electrons in the molecule, e_{el} , had to be accounted for too:

$$u = e_{tr} + e_{rot} + e_{vib} + e_{el}.$$

The difficulties were only resolved with the introduction of quantum theory. Briefly, (and very crudely) quantum theory explains that, just as matter comes in minimum sized packets called atoms, energy and angular momentum come in packets too. Packets of energy are called quanta, and the size of an energy quantum depends on the kind of energy you are dealing with. The quanta of molecular translational energy are invariably so small that the "graininess" is not apparent, and the translational energy of individual molecules can be treated as continuous, and

we have "classical" behavior, i.e. negligible quantum effects. (In an analogous way the atomic graininess of matter is usually not apparent when matter is treated in bulk and we use the continuum approximation.)

In order to speak quantitatively it is convenient to use a *characteristic temperature* θ to describe the size of a reference quantum of energy, $\varepsilon = k\theta$, where k is Boltzmann's constant ($1.38 \times 10^{-23} \text{J/K}$). Note that the quanta usually vary in size, and θ is used to describe a typical value; the energy quanta are scaled to it depending on one or more *quantum numbers*. If $T \gg \theta$, then that type of energy can be well described by classical mechanics, but if $T \sim \theta$ then non-classical effects are significant, and quantum mechanics must be used for an accurate description. The following table gives typical values of θ for each different type of molecular energy – the precise value depends on the properties of the atoms making up the molecule.

Energy type	Value of θ
Translation, θ_{tr}	$\ll 10^{-10} \text{K}$ (depends on molecular mass and size of the gas container; the larger the containment volume the smaller the value of θ_{tr})
Rotation, θ_{rot}	$\sim 0.5 - 2 \text{K}$ (except 85K for H_2)
Vibration, θ_{vib}	$\sim 1000 - 3000 \text{K}$ for most diatomics
Electronic, θ_{el}	$\sim 10,000 - 100,000 \text{K}$

The miniscule typical value of θ_{tr} emphasizes that quantum effects in translation are completely negligible at ordinary temperatures, unless the molecule is confined in a container of atomic dimensions like a *very* thin film. Hence $e_{tr} = \frac{3}{2}RT$. We see that rotational quanta are also quite small, so that at ordinary temperatures, rotation also behaves classically, i.e. $e_{rot} = RT$. (Hydrogen gas is the common exception, and quantum mechanics explains *why* it is unusual.) However, the vibrational quanta are usually large and electronic quanta are even bigger. Hence they behave non-classically.

To predict the vibrational energy and the corresponding vibrational specific heat one needs a model for the molecular vibration. If, as a simple approximation, one assumes that the molecule vibrates like a simple harmonic oscillator, then quantum mechanics predicts that any single molecule can have $\varepsilon_{vib} = 0, k\theta_{vib}, 2k\theta_{vib}, 3k\theta_{vib}, \dots$ but no other values. Statistical mechanics predicts the precise probability that a randomly chosen molecule will have any one of these energies. It also predicts that the *average* vibrational energy per unit mass of a *collection* of such harmonic oscillators e_{vib} is given by:

$$e_{vib} = \frac{R\theta_{vib}}{\exp(\theta_{vib}/T) - 1}.$$

Correspondingly,

$$c_{vib} = \frac{de_{vib}}{dT} = R \left[\frac{(\theta_{vib}/2T)}{\sinh(\theta_{vib}/2T)} \right]^2.$$

For temperatures up to about 3000 K , one can assume that the energy quanta required for electronic excitation are so large that there is effectively no electronic energy. Thus $e_{el} = 0$ at all T of interest, and the corresponding electronic specific heat is also 0.

Finally, one can assemble all these results for the specific heats of a diatomic molecule:

$$\begin{aligned} c_v &= \frac{du}{dT} = \frac{de_{tr}}{dT} + \frac{de_{rot}}{dT} + \frac{de_{vib}}{dT} + \frac{de_{el}}{dT} = c_{tr} + c_{rot} + c_{vib} + c_{el} \\ &= \frac{3}{2}R + R + R \left[\frac{\theta_{vib}/2T}{\sinh(\theta_{vib}/2T)} \right]^2 + 0 = \frac{5}{2}R + R \left[\frac{\theta_{vib}/2T}{\sinh(\theta_{vib}/2T)} \right]^2 \\ c_p &= c_v + R = \frac{7}{2}R + R \left[\frac{\theta_{vib}/2T}{\sinh(\theta_{vib}/2T)} \right]^2 \end{aligned}$$

It is often convenient to write the specific heat as a sum of a low temperature limiting value and the vibrational specific heat:

$$\begin{aligned} c_p &= c_{p_low} + c_{vib}; \\ c_{p_low} &= \frac{7}{2}R \end{aligned}$$

These theoretical ideas were used to generate the model used to fit the data for the specific heat of air. Because air is a mixture of nitrogen and oxygen, there are two different quantum oscillators in air with different values of θ_{vib} . However, we only want an approximate fit to the data, since in gas turbines the combustion products are not pure air anyway. Hence, a very accurate model for c_p for high temperature air is not justified for our cycle analysis. The data can be satisfactorily fit to the equation:

$$\begin{aligned} \frac{c_p}{R} &= \frac{c_{p_low}}{R} + \frac{c_{vib}}{R} = 3.499 + \alpha \left[\frac{\theta/T}{\sinh(\theta/T)} \right]^2; \\ \alpha &= 1.037; \theta = \theta_{vib}/2 = 1582\text{ K} \end{aligned}$$

The quantity α is slightly different from unity to compensate for the fact that we are modelling two different kinds of quantum oscillators as a single oscillator. Oxygen and nitrogen have different values of θ_{vib} , and different molar masses (hence different R). This expression for $c_p(T)$ is simple enough that it can be integrated analytically to give the following expressions for $h(T)$ and Δs :

$$\begin{aligned} h(T) &= c_{p_low}T + \alpha\theta \left[\coth\left(\frac{\theta}{T}\right) - 1 \right] = c_{p_low}T + \alpha \frac{2\theta}{\exp(2\theta/T) - 1}; \\ \frac{\Delta s}{R} &= \frac{c_{p_low}}{R} \ln \frac{T_2}{T_1} - \ln \frac{p_2}{p_1} - \alpha \left[\left(\frac{\theta}{T_1} \right) \coth\left(\frac{\theta}{T_1}\right) - \left(\frac{\theta}{T_2} \right) \coth\left(\frac{\theta}{T_2}\right) + \ln \left(\frac{\sinh(\theta/T_2)}{\sinh(\theta/T_1)} \right) \right] \end{aligned}$$

In each of these equations the term multiplying α gives the contribution of the vibrational specific heat and the other term(s) give the perfect gas (constant specific heat) result.