

3.5: Thermodynamic Quantities

By a thermodynamic “quantity” I mean either a variable or a function. We have already seen that for fluids we may regard the entropy as a function of energy, volume, and number, $S(E, V, N)$, or the energy as a function of entropy, volume, and number, $E(S, V, N)$: using the term “quantity” avoids prejudging the issue of whether entropy, for example, is to be treated as a variable or a function.

It is traditional to divide thermodynamic quantities into two classes: “extensive” and “intensive”. Extensive quantities increase linearly with system size while intensive quantities are independent of system size. (You might ask, “Why can’t a quantity depend on system size in some other fashion, such as quadratically?” The answer is that this is not impossible—for example, the radius of a spherical sample increases as the cube root of the system size—but it rarely happens in practice for quantities that concern us—see problem 3.18.) Thus extensive quantities are characteristic of the sample while intensive quantities are characteristic of the substance.

Examples of extensive quantities are energy, volume, number, entropy, and the magnetization \mathbf{M} (i.e. the magnetic dipole moment of the entire sample):

$$E, \quad V, \quad N, \quad S, \quad \mathbf{M} \quad (3.5.1)$$

Examples of intensive quantities are temperature, pressure, chemical potential, and the applied magnetic field \mathbf{H} :

$$T, \quad p, \quad \mu, \quad \mathbf{H}. \quad (3.5.2)$$

If one extensive quantity is divided by another extensive quantity, the quotient is an intensive quantity. The most frequently used quantities of this type are the *number densities*, such as

$$e = \frac{E}{N}, \quad s = \frac{S}{N}, \quad \text{and} \quad v = \frac{V}{N}. \quad (3.5.3)$$

There are also *volume densities* like

$$u = \frac{E}{V}, \quad \mathcal{S} = \frac{S}{V}, \quad \text{and} \quad \rho = \frac{N}{V}. \quad (3.5.4)$$

Quantities such as E/S are also intensive, but they are rarely used and don’t have special names.

Note that in defining densities such as above, we are not making any assumptions about how the matter in the sample is arranged. For liquid water in equilibrium with ice (e.g. at atmospheric pressure and a temperature of 273 K) the water has a greater number density (and a greater entropy density) than the ice, but the number density of the system is still just the total number divided by the total volume.

Here is a valuable problem solving tip. You know from previous courses that it is important to keep track of the dimensions of physical quantities: if you derive an equation for which the left side has the dimensions of meters and the right side has the dimensions of meters/second, your derivation must be wrong. In thermodynamics there is the equally important check of extensivity: if the left side is extensive and the right side is intensive, then the equation must be wrong. You should keep a running check of these properties as you solve problems. The first time you produce an equation that is incorrect in its dimensions or its extensivity, go back immediately and correct your error.

Problem 1.2 has already introduced the “isothermal compressibility”

$$\kappa_T(p, T) = -\frac{1}{V} \frac{\partial V(p, T)}{\partial p} \quad (3.5.5)$$

and the “expansion coefficient”

$$\beta(p, T) = \frac{1}{V} \frac{\partial V(p, T)}{\partial T}. \quad (3.5.6)$$

Both of these quantities are defined so as to be intensive.

Another quantity of interest is the “heat capacity”, defined informally as “the amount of heat required to quasistatically raise the temperature of a sample by one kelvin”. (The heat capacity was introduced briefly in problem 1.3.) Because this definition refers to a sample, heat capacity is an extensive quantity. The definition is incomplete because it doesn’t say what path is taken while the heat is added, and we know that heat is a path-dependent quantity.¹ For fluids, the two most frequently used heat capacities are the heat capacity at constant volume and at constant pressure, denoted by

$$C_V \text{ and } C_p. \quad (3.5.7)$$

Thus C_p (which will in general be a function of temperature, pressure, and number) is the amount of heat required to increase the temperature of a sample by one kelvin while the sample is under a constant pressure (often, in earth-bound laboratories, a pressure of one atmosphere). In contrast C_V (which will in general be a function of temperature, volume, and number) is the amount of heat required to increase the temperature of a sample by one kelvin while holding it in a strong box to prevent it from expanding. Because liquids expand little upon heating, C_V and C_p are nearly equal for liquids. But the two quantities differ dramatically for gases.

For small quasistatic changes, we know that

$$\Delta S = \frac{Q}{T} \quad (3.5.8)$$

whence

$$C = \lim_{\Delta T \rightarrow 0} \frac{T \Delta S}{\Delta T}. \quad (3.5.9)$$

This gives us the formal definitions of heat capacity,

$$C_V = T \frac{\partial S(T, V, N)}{\partial T} \quad \text{and} \quad C_p = T \frac{\partial S(T, p, N)}{\partial T}, \quad (3.5.10)$$

and from these equations it is again clear that heat capacity is an extensive quantity.

The intensive quantities analogous to heat capacities are called “specific heats”:

$$c_V = \frac{C_V}{N} \quad \text{and} \quad c_p = \frac{C_p}{N}. \quad (3.5.11)$$

The specific heat is readily measured experimentally and we will come back to it again and again.

Problems

3.14 (E) Which one was it?

For a system with a fixed number of particles, the reciprocal of the absolute (kelvin) temperature T is given by which of the following derivatives? Explain your reasoning. Do not look up the answer or, if you have memorized it, don’t use that piece of your memory. (Clue: Dimensional analysis will work, but there’s an even easier way.)

$$\frac{\partial p(S, V)}{\partial V} \quad \frac{\partial p(S, V)}{\partial S} \quad \frac{\partial S(E, p)}{\partial p} \quad \frac{\partial V(E, p)}{\partial p} \quad \frac{\partial S(E, V)}{\partial E} \quad (3.5.12)$$

3.15 (I) Acceptable forms for the entropy

Below are seven equations purporting to be equations for $S(E, V, N)$ for various thermodynamic systems. However, four of them are not physically acceptable. Find the four impermissible equations and for each indicate why it cannot be correct. The quantities T_0 and v_0 are in all cases positive, intensive quantities with the dimensions of temperature and volume, respectively.

$$S(E, V, N) = \left(\frac{k_B^2}{v_0 T_0} \right)^{1/3} (EVN)^{1/3} \quad (3.5.13)$$

$$S(E, V, N) = \left(\frac{k_B v_0^2}{T_0^2} \right)^{1/3} \left(\frac{EN}{V} \right)^{2/3} \quad (3.5.14)$$

$$S(E, V, N) = \left(\frac{k_B v_0^2}{T_0^2} \right)^{1/3} \frac{EN}{V} \quad (3.5.15)$$

$$S(E, V, N) = \left(\frac{k_B}{T_0} \right)^{1/2} \left(NE + \frac{k_B T_0 V^2}{v_0^2} \right)^{1/2} \quad (3.5.16)$$

$$S(E, V, N) = k_B N \ln(EV / N^2 k_B T_0 v_0) \quad (3.5.17)$$

$$S(E, V, N) = k_B N \exp(-EV / N^2 k_B v_0) \quad (3.5.18)$$

$$S(E, V, N) = k_B N \exp(-EV^2 / N^2 k_B T_0 v_0^2) \quad (3.5.19)$$

3.16 (I) Heat capacities for the ideal gas

Use equation (2.32) to find the heat capacities

$$C_V(T, V, N) = T \left(\frac{\partial S}{\partial T} \right)_{V, N} \text{ and } C_p(T, p, N) = T \left(\frac{\partial S}{\partial T} \right)_{p, N}$$

for the pure classical monatomic ideal gas.

3.17 (I) Heat capacity at a phase transition

What is C_p for a fluid when the liquid and gas coexist?

3.18 (D) Gravitational potential energy

Consider a uniform sphere of mass M and radius R .

- a. Use dimensional analysis to show that the gravitational potential energy of the sphere is of the form

$$U_G = -cG \frac{M^2}{R}, \quad (3.5.20)$$

where c is a dimensionless constant independent of M and R .

- b. Is U_G intensive, extensive, or neither?

- c. Is the total energy E (which is equal to U_G plus contributions from other forms of energy) intensive, extensive, or neither?

- d. Estimate the value of U_G for a glass of water.

You should conclude from this problem that the total energy E is in principle non-extensive, but that the deviations from being extensive are negligible for everyday thermodynamic systems.

- e. (Optional and quite time consuming.) Use ideas from classical mechanics to show that the dimensionless constant in equation (3.60) is $c = 3/5$.

¹In truth, it's worse than this, because it doesn't even specify the end point of the process. If we are describing the fluid sample by V and T , for example, and the starting point were (V_i, T_i) , then the end point must have $T_f = T_i + 1$ K, but as far as our informal definition goes, the final volume could be anything.