

HEAT CAPACITIES AT CONSTANT VOLUME AND PRESSURE

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problems 1.44 - 1.45.

The heat capacity of a substance is defined as

$$(1) \quad C \equiv \frac{Q}{\Delta T} = \frac{\Delta U - W}{\Delta T}$$

The heat capacity thus depends on whether any work was done on the substance to change its temperature. If there is no work ($W = 0$), then usually the volume of the sample doesn't change. In that case, we can measure the heat capacity at constant volume:

$$(2) \quad C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

where the subscript V on the partial derivative indicates that V is held constant.

Example. Although I imagine most readers are familiar with partial derivatives, I'll include this problem from Schroeder for completeness. Suppose we have a couple of functions

$$(3) \quad w = xy$$

$$(4) \quad x = yz$$

The variable w can be viewed as a function of any two of x , y and z :

$$(5) \quad w = xy = y^2z = \frac{x^2}{z}$$

A couple of partial derivatives are

$$(6) \quad \left(\frac{\partial w}{\partial x} \right)_y = y$$

$$(7) \quad \left(\frac{\partial w}{\partial x} \right)_z = \frac{2x}{z} = 2y$$

Thus it is not enough just to say that we're taking the partial derivative of w with respect to x ; we must also say which of the other two variables is held constant.

The remaining partials are

$$(8) \quad \left(\frac{\partial w}{\partial y}\right)_x = x$$

$$(9) \quad \left(\frac{\partial w}{\partial y}\right)_z = 2yz = 2x$$

$$(10) \quad \left(\frac{\partial w}{\partial z}\right)_x = -\frac{x^2}{z^2}$$

$$(11) \quad \left(\frac{\partial w}{\partial z}\right)_y = y^2 = \frac{x^2}{z^2}$$

Now suppose that the pressure on the substance is constant as heat is added to it. Most substances expand when they are heated, so the substance does work $P\Delta V$ on its surroundings as it is heated. In this case, some of the heat added to the substance is converted to the work done on the surroundings, so not all of the added heat goes to increasing the temperature of the substance. The thermal energy change is thus $\Delta U = Q - P\Delta V$ and we can define the heat capacity at constant pressure as

$$(12) \quad C_P \equiv \left(\frac{Q}{\Delta T}\right)_P = \left(\frac{\Delta U + P\Delta V}{\Delta T}\right)_P$$

Taking the limit, we get

$$(13) \quad C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

This isn't directly comparable with C_V from 2, since $\frac{\partial U}{\partial T}$ is taken with different quantities held constant, but usually $C_P > C_V$ because of the heat lost as work.

For substances whose thermal energy is entirely in the form of quadratic degrees of freedom, $U = \frac{1}{2}NfkT$ and

$$(14) \quad C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_P = \frac{1}{2}Nfk = \frac{1}{2}nRf$$

where n is the number of moles and R is the gas constant.

For an ideal gas at constant pressure

$$(15) \quad \left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial}{\partial T} \left(\frac{NkT}{P}\right) = \frac{Nk}{P}$$

$$(16) \quad C_P = \left(\frac{\partial U}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P$$

$$(17) \quad = \left(\frac{\partial U}{\partial T}\right)_V + Nk$$

$$(18) \quad = C_V + Nk$$

$$(19) \quad = C_V + nR$$

$$(20) \quad = nR \left(\frac{f}{2} + 1\right)$$

In SI units, $R = 8.31 \text{ J mol}^{-1}\text{K}^{-1}$ so for one mole for an ideal gas

$$(21) \quad C_P = 8.31 \left(1 + \frac{f}{2}\right)$$

For monatomic gases

$$(22) \quad C_P = 8.31 \times \frac{5}{2} = 20.775$$

From the table in the appendix to Schroeder's book, this is in excellent agreement with the values for argon, helium and neon.

For diatomic gases with translational and rotational degrees of freedom

$$(23) \quad C_P = 8.31 \times \frac{7}{2} = 29.085$$

which is quite close to the values for O_2 , N_2 and H_2 and CO .

For most solids and liquids, $\left(\frac{\partial V}{\partial T}\right)_P$ is quite small so we'd expect

$$(24) \quad C_P \approx 8.31 \frac{f}{2}$$

For a solid, there are a possible 9 degrees of freedom (3 translational and 6 vibrational). However, if we assume that atoms are locked into a crystal lattice so the translational degrees of freedom don't contribute much then $f = 6$ and

$$(25) \quad C_P \approx 24.93$$

This is quite close to the values for elemental metals such as aluminum, copper, iron and lead.

More complex compounds tend to have much higher heat capacities, but here there are a lot of complex interactions going on so we wouldn't expect the simple theory to apply very well.

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