Entropy as a function

Entropy was presented as a function, particularly in its non-molecular, phenomenological exposition. What does this function look like? First of all, there is no single function; such a function is a constitutive function specific for a specific body (material). Often, its explicit form comes from some molecular insight.

One well-known example is the **Sackur-Tetrode equation** derived for a monoatomic ideal gas consisting of N atoms on the basis of statistical theory (Grimus, 2013)[1]:

$$\frac{S}{kN} = \ln\left[\frac{V}{N}\left(\frac{4\pi m}{3h^2}\frac{E}{N}\right)^{3/2}\right] + \frac{5}{2}. \tag{1}$$

It is thus not given as a function of our preferred variables, temperature and volume, but in terms of volume (V) and kinetic (internal) energy (E); because of the direct link between the kinetic energy of ideal gas atoms and temperature, this is an irrelevant difference. The symbol h is the Planck's constant, k the Boltzmann constant, and m the mass of the atom.

Another (almost) explicit function was published by Giovangigli & Massot (1998) and Yong (2007) for the specific entropy s_k of a component k of a mixture:

$$s_k(\rho_k, T) = s_k^{00} + \int_{T_0}^{T} \frac{c_{vk}(T')}{T} dT' - r_k \log\left(\frac{\rho_k}{\gamma_0 m_k}\right). \tag{2}$$

Instead of volume, there is the density ρ_k. This is inevitable in a non-uniform mixture (cf., e.g., sec. 4.2 in Pekař & Samohýl, 2014); the density is called mass concentration in chemistry and is introduced using volume. There is the additive constant s_k^{00}; to solve the integral, the temperature dependence of the specific heat capacity $c_{vk}(T')$ should be known. The equation was derived from the kinetic theory of dilute polyatomic gas mixture.

The thermal properties of individual substances are often presented in terms of polynomial expansions. Water was mentioned in the book as a special substance. The NIST database (Linstrom & Mallard, 2024) gives the following equation for the standard molar entropy of gaseous water

$$S^\circ = A \ln t + B\, t + C\, t^2/2 + D\, t^3/3 - E/(2t^2) + G, \tag{3}$$

where $t = T/1000$. A to G are constants, the values of which can be found in the database (Linstrom & Mallard, 2024). Remember that the value of the standard pressure (0.1 MPa) is constant, there is no information on the dependence on volume, and eq. (3) can be viewed as expressing entropy as a function of temperature and pressure but given for a specific value of the pressure. This equation is based on data published in Chase (1998), where interested readers can find data for other substances (as well as for liquid water) and make their own (polynomial) fits.

In sec. 9.8 of our book, we showed how the change in entropy can (easily) be calculated in isochoric processes using the heat capacity at constant volume. This indicates a procedure for finding a function for "isochoric entropy". In the case of a monoatomic ideal gas, its (average) molar heat capacity at constant volume is temperature independent and given by $C_{Vm} = (3/2)R$ (McQuarrie & Simon, 1997). Then, referring to eq. (9.62) in our book, we have

$$S_m\big(T(t_2)\big) = S_m\big(T(t_1)\big) + \frac{3}{2} R \ln\frac{T(t_2)}{T(t_1)} \quad (V = \text{const.}). \tag{4}$$

Thus, the molar entropy S_m is given (under isochoric conditions) as a function of temperature, which, in turn, is a function of time. The value $S_m\big(T(t_1)\big)$ can be viewed as an additive constant.

In the case of a biatomic gas, the expression is more complex and temperature-dependent (McQuarrie & Simon, 1997):

[1] We keep the symbols used in the original sources although they sometimes differ from those used in our book.

$$C_{Vm} = \frac{5}{2}R + R\left(\frac{h\nu}{kT}\right)^2 \frac{\exp\left(-h\nu/kT\right)}{[1-\exp(-h\nu/kT)]^2}. \tag{5}$$

The integration of eq. (9.61) in the book is thus not straightforward and is not developed here. Using the molar mass of a particular gas, the specific heat capacity can be expressed from eq. (5) and substituted in eq. (2).

McQuarrie & Simon (1997) also present Einstein's model of an atomic crystal for which they derive:

$$C_{Vm} = 3R\left(\frac{h\nu}{kT}\right)^2 \frac{\exp\left(-h\nu/kT\right)}{[1-\exp(-h\nu/kT)]^2}. \tag{6}$$

This expression, quite similar to (5), is also temperature-dependent.

Expressions (functions) can also be found for the C_V of water. Amirchanov et al. (1974) give a polynomial function for gaseous water in the range 500-800 °C and 0-1000 bar:

$$C_V = C_{V0} + a\,\frac{p}{100} + b\left(\frac{p}{100}\right)^2 - c\left(\frac{p}{100}\right)^3 + d\left(\frac{p}{100}\right)^4, \tag{7}$$

where the coefficients are functions of temperature (t, in °C probably, the original symbols are rather confusing), e.g.

$$a = a_0 + a_1\,\frac{t}{100} + a_2\left(\frac{t}{100}\right)^2 - a_3\left(\frac{t}{100}\right)^3,$$

Here a_i are constants given in the original source. A similar equation is also given for liquid water (100-350 °C and 25-1000 bar); it is simpler – it contains no third- or fourth-degree terms.

An integro-exponential expression was published for solid water (ice VII) by Myint et al. (2017):

$$C_V = 9R\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 \exp\left(x\right)}{[\exp(x)-1)]^2}\,dx, \tag{8}$$

where θ_D is the Debye temperature (1470 K), together with an analytical expression for the integral.

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