

ENTROPY OF WATER AND STEAM

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problems 4.27 - 4.28.

For a steam engine, Schroeder gives enthalpy and entropy values for water and steam at the boiling point for various pressures (his Table 4.1). What may at first seem a bit odd is that the entropy for liquid water increases with temperature, but that for steam *decreases* with increasing temperature.

The key point is that the entropy values are given for a fixed amount (1 kg) of water or steam. As the pressure is increased on liquid water, its volume changes very little, so the increase in temperature means that temperature is the only state variable of the water that changes. This gives rise to more molecular motion, hence more randomness, hence larger entropy.

For steam, the increase in temperature is accompanied by an increase in pressure (since the boiling point of water increases with increasing pressure) and, since the number of water molecules is constant, the volume of the steam (a gas) reduces considerably as the pressure is increased. Thus there is an increase in entropy due to increasing temperature, but also a decrease due to the decreasing volume.

At low pressures such as those quoted in Table 4.1, it's not too bad an approximation to take steam as an ideal gas, so we can apply the Sackur-Tetrode equation to get a feel for how the entropy changes. The equation says

$$(0.1) \quad S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right]$$

The energy U is (from the equipartition theorem)

$$(0.2) \quad U = \frac{f}{2} NkT$$

The volume is

$$(0.3) \quad V = \frac{NkT}{P}$$

so the equation becomes

$$(0.4) \quad S = Nk \left[\ln \left(\frac{(kT)^{5/2}}{P} \left(\frac{4\pi fm}{6h^2} \right)^{3/2} \right) + \frac{5}{2} \right]$$

For a few of the values of T and P given in Table 4.1, the ratio $T^{5/2}/P$ is

T (K)	P (bar)	$T^{5/2}/P$
273	0.006	2.05×10^8
283	0.012	1.12×10^8
373	1.013	2.65×10^6

The units of $T^{5/2}/P$ aren't particularly important here; what matters is that this quantity decreases as we move down the table, so the entropy will actually decrease as we increase the pressure.

In a related problem, Schroeder claims that we can reconstruct the entropy values in Table 4.1 from the given enthalpy values. I'm not entirely sure how he expects us to do it, but it does seem to require some approximations. From the definition of entropy we have

$$(0.5) \quad S = \frac{Q}{T}$$

where Q is the heat absorbed or lost by the substance at constant temperature T . The enthalpy is the energy required to create the substance from nothing at constant pressure. For the first row in the table, we can imagine the steam being created at constant pressure at $T = 0^\circ \text{C} = 273.15 \text{K}$ so the entropy is

$$(0.6) \quad S = \frac{Q}{T} = \frac{H_{\text{steam}}}{T} = \frac{2501}{273.15} = 9.156 \text{ kJ kg}^{-1} \text{K}^{-1}$$

which agrees with the value in the table.

To get the second row, we can look at the liquid water first. In this case, we heat the water from 0°C to 10°C while increasing the pressure from 0.006 bar to 0.012 bar (with 1 bar = 10^5N m^{-2}), so both the temperature and pressure are changing from their values in the first row, so it's no longer a constant pressure process. The enthalpy change in this case is

$$(0.7) \quad dH = Q - PdV + d(PV) = Q + VdP$$

A kilogram of water has a volume of $V = 10^{-3} \text{m}^3$ and this changes very little as the pressure is increased, so the VdP term is

$$(0.8) \quad VdP \approx 10^{-3} \times 0.006 \times 10^5 = 0.6 \text{ J}$$

Compared to the value $dH = 42 \times 10^3$ J, this correction can be neglected, so to a good approximation

$$(0.9) \quad S_{water} = \frac{dH}{T}$$

However, T is also changing so what value do we use for it? It seems that a reasonable approximation is to use the average value, so we get

$$(0.10) \quad S_{water} = \frac{42}{278} = 0.151 \text{ kJ kg}^{-1}\text{K}^{-1}$$

which again agrees with the value in the table.

The value for steam is a bit more difficult to estimate. If we take the steam to be an ideal gas and apply the thermodynamic identity, we get

$$(0.11) \quad dH = TdS + VdP$$

$$(0.12) \quad dS = \frac{1}{T}(dH - VdP)$$

From the ideal gas law

$$(0.13) \quad V = \frac{nRT}{P}$$

$$(0.14) \quad dS = \frac{dH}{T} - nR\frac{dP}{P}$$

However, now all three of V , P and T are changing so it seems the best we can do is to use the average values. To go from the first row to the second row in the table, we have $dH = 19$ kJ, $dP = 0.006$ bar, $P = 0.009$ bar, $T = 278$ K. 1 kg of steam is equivalent to $n = 55.5$ mol (the molar weight of water is 18.01 g) and the gas constant is $R = 8.314$ in SI units. Plugging in all the numbers gives

$$(0.15) \quad dS = -0.239 \text{ kJ kg}^{-1}\text{K}^{-1}$$

$$(0.16) \quad S_{steam} = 8.917 \text{ kJ kg}^{-1}\text{K}^{-1}$$

This is off by 0.016 from the value in the table, but considering the number of approximations, I suppose it's not bad.

We can actually get a slightly better approximation by taking the average of $\frac{1}{T}$ and $\frac{1}{P}$ by using the integral formula for the average of a function $f(x)$ over the domain $x_1 \leq x \leq x_2$:

$$(0.17) \quad \langle f(x) \rangle = \frac{1}{x_2 - x_1} \int_{x_1}^{x_2} f(x) dx$$

For $f(x) = \frac{1}{x}$ we get

$$(0.18) \quad \left\langle \frac{1}{x} \right\rangle = \frac{1}{x_2 - x_1} \ln \frac{x_2}{x_1}$$

We then get, for values between the first and second rows of the table

$$(0.19) \quad \left\langle \frac{1}{T} \right\rangle = \frac{1}{10} \ln \frac{283}{273} = 3.60 \times 10^{-3}$$

$$(0.20) \quad \left\langle \frac{1}{P} \right\rangle = \frac{1}{0.006} \ln \frac{0.012}{0.006} = 115.5$$

With these values, we get, in SI units

$$(0.21) \quad dS = dH \left\langle \frac{1}{T} \right\rangle - nRdP \left\langle \frac{1}{P} \right\rangle$$

$$(0.22) \quad = 68.4 - 319.8$$

$$(0.23) \quad = -251.4 \text{ J K}^{-1}$$

$$(0.24) \quad = -0.2514 \text{ kJ K}^{-1}$$

$$(0.25) \quad S_{steam} = 8.905 \text{ kJ kg}^{-1} \text{K}^{-1}$$

This reduces the discrepancy to 0.004.