Vagaries in the Statistical Definition of the Entropy

- The statistical definition of the entropy appears in many forms; almost every textbook finds its own version - and all versions are equally correct. You will always find the definition

$$\boxed{S = k \cdot \ln P}$$

- But the meaning of ***P*** may be quite different on a first glance. Let's look at a few examples:

Basics

- "***P*** means the probability of a macrostate, where ***P*** in turn is proportional to the number of microstates accessible to the system contained within that macrostate".
  - The quote is from: *R.P. Baumann*; Modern Thermodynamics with Statistical Mechanics, p. 337.
  - Note that a probability is a number ≤ 1; S thus would be always negative.
- ***P*** is the volume in **phase space** occupied by the system.
  - *Becker*, Theorie der Wärme, S. 117 (That's what I had as a student).
  - Note that this looks like a number with a dimension!
- Now some random finds without the detailed quote.
- ***P*** is the number of indistinguishable microstates belonging to one macrostate.
  - That is the definition we used in the script. Note that this is a pure, and mostly very large number.
- ***P*** is the probability for a macrostate, i.e. the number P_i of microstates belonging to a certain macrostate **i** divided by the sum over all possible P_i.
  - Note that P than is a pure number between **0** and **1**.
- What is correct? The numerical value of S obviously could be positive or negative and generally very different depending on which definition one uses.
  - The answer, of course, draws on the old fact that in classical physics (including thermodynamics) there is *no absolute scale* for energies (and entropy times temperature is a form of energy).
  - We thus can always use a P^* instead of P, defined by $P^* = P/P_0$ with P_0 = arbitrary constant factor (that does not depend on the variables of the system under consideration). All that happens is that you add a constant factor to the entropy or free energy of a system; i.e. you change the zero point of the energy scale.
  - If we replace P by P^*, we obtain for the entropy .

$$\boxed{S^* = k \cdot \ln P^* = k \cdot \ln \frac{P}{P_0} = k \cdot \ln P - k \cdot \ln P_0 = S - \text{const.}}$$

  - For the free enthalpy we then simply have $G^* = G - kT \cdot \ln P_0 = G - \text{const}$
  - Moreover, since in practice most applications contain the derivative of S with respect to some variable x of the system, constant factors will disappear, i.e..

$$\boxed{\frac{\partial S^*}{\partial x} = \frac{\partial S}{\partial x}}$$

- In short, all definitions are equivalent and you don't have to worry about the additional constant factors that may appear. Feel free to use the definition that is most easily applied to the problem under consideration.
  - However, if you *like* to worry, or noticed that there was a little disclaimer above, read on in the advanced section.