

Addendum to “Entropy as Disorder”: What about Gibbs potential?

Dan Styer, Oberlin College, Oberlin, OH; 10 February 2020

After the publication of “Entropy as Disorder: History of a Misconception” [*The Physics Teacher*, volume 57, pages 454–458 (October 2019); erratum volume 58, page 5 (January 2020)] I got a number of questions like “Why do you focus on entropy? Isn’t enthalpy, or Gibbs potential,¹ more appropriate?” This is a good question, and this addendum essay answers it.

It is certainly true² that the equilibrium criterion differs under different conditions:

under these conditions ...	the equilibrium macrostate ...
fixed energy, volume, and number	maximizes entropy $S(U, V, N)$
fixed temperature, volume, and number	minimizes Helmholtz potential $A(T, V, N)$
fixed temperature, pressure, and number	minimizes Gibbs potential $G(T, p, N)$
fixed entropy, volume, and number	minimizes energy $U(S, V, N)$
fixed entropy, pressure, and number	minimizes enthalpy $H(S, p, N)$
fixed temperature, volume, and chemical potential	maximizes pressure $p(T, \mu)$

And it is certainly true that these are very different mathematical procedures.

¹Sometimes the questioner uses the term “free energy”. Both the International Union of Pure and Applied Physics and the International Union of Pure and Applied Chemistry depreciate the use of this term. [See IUPAP, SUNAMCO Commission, “Symbols, Units, Nomenclature and Fundamental Constants in Physics: 1987 Revision” (prepared by E. Richard Cohen and Pierre Giacomo) *Physica* **146A** (1987) 1-68, section 4.4 “Recommended Symbols for Physical Quantities: Thermodynamics” and IUPAC, *Compendium of Chemical Terminology*, second edition (the “Gold Book”, compiled by A.D. McNaught and A. Wilkinson, 1997).] IUPAP recommends “Gibbs [or Helmholtz] function”. IUPAC recommends “Gibbs [or Helmholtz] energy”. Following Arnold Sommerfeld [*Lectures on Theoretical Physics, volume V: Thermodynamics and Statistical Mechanics* (edited by F. Bopp and J. Meixner, translated by J. Kestin, Academic Press) pages v, 44, 349, 362] I prefer the name “Gibbs [or Helmholtz] potential”.

²See, for example, Herbert B. Callen, *Thermodynamics* (John Wiley, New York, 1960) sections 5.1, 6.1.

But the surprising result is that these different procedures result in the same equilibrium macrostates. For example:

A sealed bottle of salad dressing is at a fixed volume and the pressure fluctuates (minutely). The equilibrium macrostate is determined by minimizing $A(T, V, N)$.

When the lid is unscrewed, the salad dressing is at fixed pressure and the volume fluctuates (minutely). Now the equilibrium macrostate is determined by minimizing $G(T, p, N)$.

But anyone who has ever unscrewed a bottle of salad dressing knows that the dressing doesn't change when the lid is unscrewed: it remains in the same equilibrium macrostate. The results of these two very different mathematical procedures are identical.

Or again:

A sealed bottle of salad dressing is at a fixed temperature and the energy fluctuates (minutely). The equilibrium macrostate is determined by minimizing $A(T, V, N)$.

When the bottle is placed within a thermos, the salad dressing is at fixed energy and the temperature fluctuates (minutely). Now the equilibrium macrostate is determined by maximizing $S(U, V, N)$.

But anyone who has worked with salad dressing knows that the dressing doesn't change when placed within a thermos: it remains in the same equilibrium macrostate. The results of these two very different mathematical procedures are identical.

The fancy name³ applied to this straightforward result is "equivalence of ensembles in the thermodynamic limit".

So to get a handle on these various situations – fixed volume vs. pressure – one must get a handle on the various potentials – Helmholtz vs. Gibbs. And this is best done by getting a handle on entropy, as my paper seeks to do.

³David Ruelle, *Statistical Mechanics: Rigorous Results* (W.A. Benjamin, Reading, Massachusetts, 1969) sections 3.3, 3.4.