HELMHOLTZ ENERGY OF A HYDROGEN ATOM

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 5.20.

The Helmholtz energy is defined as

$$F \equiv U - TS \tag{1}$$

We can apply this to a hydrogen atom, at least in an approximate form. The ground state of hydrogen has quantum numbers $n = 1$, $\ell = m = 0$ and is non-degenerate. The first excited state is four-fold degenerate, as its quantum numbers are $n = 2$ with $\ell = m = 0$ or $\ell = 1$ and $m = \pm 1, 0$. We can therefore say that the entropy of the $n = 2$ state is

$$S = k \ln 4 \tag{2}$$

with $k = 8.62 \times 10^{-5}$ eV K^{-1}.

If we take the energy of the ground state to be zero, then the first excited state has $U = 10.2$ eV. The Helmholtz energy is therefore zero at a temperature of

$$T_0 = \frac{U}{S} = \frac{10.2}{(8.62 \times 10^{-5}) \ln 4} = 8.54 \times 10^4 \text{ K} \tag{3}$$

For $T > T_0$, $F < 0$ so the excited state is actually the preferred state, and a hydrogen atom in the ground state would spontaneously make the transition to the excited state. However, T_0 is so large that virtually all hydrogen atoms would be ionized at that temperature, as we saw earlier when discussing the Saha equation for stellar atmospheres. We saw there that the fraction of hydrogen atoms that are ionized is essentially 1.0 for temperatures above around 12000 K.