

GRAND FREE ENERGY

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 5.23.

If we subtract μN from the existing thermodynamic potentials U , H , F or G we get yet more thermodynamic potentials (as if we needed even more of them). The *grand free energy* or *grand potential* is defined by

$$(1) \quad \Phi \equiv F - \mu N = U - TS - \mu N$$

The thermodynamic identity for Φ is

$$(2) \quad d\Phi = dU - T dS - S dT - \mu dN - N d\mu$$

The full thermodynamic identity for U is

$$(3) \quad dU = T dS - P dV + \mu dN$$

so

$$(4) \quad d\Phi = -P dV - S dT - N d\mu$$

The corresponding partial derivatives are

$$(5) \quad \left(\frac{\partial \Phi}{\partial V} \right)_{T, \mu} = -P$$

$$(6) \quad \left(\frac{\partial \Phi}{\partial T} \right)_{V, \mu} = -S$$

$$(7) \quad \left(\frac{\partial \Phi}{\partial \mu} \right)_{T, V} = -N$$

Schroeder asks us to prove that for a system in thermal and diffusive equilibrium with a reservoir, Φ tends to decrease. I suspect he would use a derivation similar to that leading up to his equation 5.29 for F , but as I don't trust that method, I'll use the method that deals with the total entropy of the system. As before, the total entropy of the system + reservoir is

$$(8) \quad S_{total} = S + S_R$$

At equilibrium, S_{total} must be a maximum, from the second law. The energies obey the relation

$$(9) \quad U_{total} = U + U_R$$

And the volumes:

$$(10) \quad V_{total} = V + V_R$$

And the numbers:

$$(11) \quad N_{total} = N + N_R$$

Since the system is allowed to exchange only energy and number with the reservoir, we can take V and V_R to be constants. The entropy of the reservoir is built up from contributions from U , V and N , so we have

$$(12) \quad S_R = \frac{U_R}{T} + P \frac{V_R}{T} - \mu \frac{N_R}{T}$$

where the last term comes from the definition of chemical potential

$$(13) \quad \mu \equiv -T \left(\frac{\partial S}{\partial N} \right)_{U,V}$$

Therefore the total entropy is

$$(14) \quad S_{total} = S + \frac{1}{T} [U_{total} - U + P(V_{total} - V) - \mu(N_{total} - N)]$$

$$(15) \quad = S - \frac{1}{T} (U - \mu N) + \frac{1}{T} [U_{total} + P(V_{total} - V) - \mu N_{total}]$$

The last term in square brackets is constant, so to maximize S_{total} we must maximize the first two terms. That is

$$(16) \quad \max [S_{total}] = \max \left[-\frac{1}{T} (U - TS - \mu N) \right] + \frac{1}{T} [U_{total} + P(V_{total} - V) - \mu N_{total}]$$

Because of the minus sign in the first term on the RHS, this is equivalent to *minimizing* $U - TS - \mu N = \Phi$.

We can actually write Φ in a simpler form. The Gibbs energy is

$$(17) \quad G \equiv U + PV - TS$$

and for a system at constant temperature and pressure, it is also

$$(18) \quad G = N\mu$$

so we can write

$$(19) \quad \Phi = U - TS - \mu N$$

$$(20) \quad = G - PV - \mu N$$

$$(21) \quad = \mu N - PV - \mu N$$

$$(22) \quad = -PV$$

As an example of a system that can exchange energy and number with a reservoir, Schroeder proposes a single proton in the Sun's atmosphere. The proton can exist in one of two states: with a bound electron (where the energy of the electron is -13.6 eV) or without a bound electron (where the energy is taken to be zero). The system in this case can be in a state where the number of electrons present is $N = 1$ (when one is bound to the proton) or $N = 0$ (the proton is alone). Ignoring all the other possible states (the excited states of the hydrogen atom, and the two spin states of the electron), each of these states has only one microstate, so both states have zero entropy: $S = 0$.

The $N = 0$ state therefore has

$$(23) \quad \Phi_0 = U - TS - \mu N$$

$$(24) \quad = 0 - 0 - 0 = 0$$

To work out Φ_1 for the $N = 1$ state, we need to know μ which we can get by taking the electrons in the solar atmosphere to be an ideal gas. The chemical potential of an ideal gas is

$$(25) \quad \mu = -kT \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right]$$

If we take the temperature of the solar atmosphere to be $T = 5800$ K and the number density of electrons to be $\frac{N}{V} = 2 \times 10^{19} \text{ m}^{-3}$, then we can work out μ :

(26)

$$\mu = -\left(8.617 \times 10^{-5} \text{eV K}^{-1}\right) (5800 \text{ K}) \times$$

(27)

$$\ln \left[\left(\frac{1}{2 \times 10^{19} \text{ m}^{-3}} \right) \left(\frac{2\pi (9.11 \times 10^{-31} \text{ kg}) (1.38 \times 10^{-23} \text{ J K}^{-1}) (5800 \text{ K})}{(6.63 \times 10^{-34} \text{ J s})^2} \right)^{3/2} \right]$$

(28)

$$= -8.89 \text{ eV}$$

(29)

$$\Phi_1 = -13.6 + 8.89 = -4.71 \text{ eV}$$

At this temperature, the bound state has a lower Φ so is more stable. This is actually consistent with the Saha equation which predicts very little ionization of hydrogen at $T = 5800 \text{ K}$.

To find the temperature where both states are equally stable, we need to find T such that $\mu = -13.6 \text{ eV}$. As T appears both inside and outside the logarithm, this is a transcendental equation which we can solve numerically. Using Maple to do this, we obtain $T = 8588 \text{ K}$. The Saha equation predicts 50% ionization at $T = 9558 \text{ K}$ so this isn't a bad estimate considering how crude the model is.