

## GIBBS AND HELMHOLTZ FREE ENERGIES; THERMODYNAMIC POTENTIALS

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 5.1.

One of the confusing things about thermodynamics is the number of energy functions in use. We've already met the internal (kinetic) energy  $U$  and the enthalpy, defined as

$$(0.1) \quad H \equiv U + PV$$

The enthalpy is the total energy required to create the system from nothing, in which the environment at constant pressure  $P$  must be pushed back to create the volume  $V$  in which the new system is to be stored. Thus the enthalpy is effectively the energy of the system in constant pressure environments.

The Helmholtz free energy  $F$  (other sources call it  $A$ ) is defined as

$$(0.2) \quad F \equiv U - TS$$

Schroeder's description of this definition is rather vague, since he claims that  $F$  is the work required to create a system out of nothing, if the system is in contact with a thermal reservoir so that its temperature is held constant at  $T$ . This arises because for isothermal, reversible processes, the entropy absorbed from a thermal reservoir is  $S = Q/T$ , so  $TS = Q$  is the contribution of the reservoir to the total energy  $U$ ; thus the difference  $U - TS$  must be the work required to produce the system.

However, in the definition of enthalpy, the total energy of a system created at constant pressure is the *sum* of  $U$  and the work  $PV$  required to make room for the system by pushing back the atmosphere. Thus it would seem that  $U$  excludes the work  $PV$  required to make room for the system.

Other sites on the web point out that  $F$  is actually the work required to create the system at constant temperature *and constant volume*. That is, space has already been cleared for the system, which is then placed in contact with the reservoir so it can absorb the heat  $TS$ . Any extra energy required to top up the total energy to the value  $U$  must then be provided

by doing work (for example, electrical work, which doesn't change the volume) on the system.

The Gibbs free energy is then defined as the Helmholtz free energy plus the work  $PV$  required to make room for the system at constant pressure:

$$(0.3) \quad G \equiv F + PV = U - TS + PV$$

The four energies  $U$ ,  $H$ ,  $F$  and  $G$  are known as *thermodynamic potentials*.

As an example, we'll look at one mole of argon gas at room temperature (298 K) and atmospheric pressure (1 bar  $\approx 10^5$  Pa). We've already worked out  $U$ ,  $S$  and  $V$  for this system:

$$(0.4) \quad U = 3739 \text{ J}$$

$$(0.5) \quad S = 155 \text{ J K}^{-1}$$

$$(0.6) \quad V = 0.025 \text{ m}^3$$

The other potentials are

$$(0.7) \quad H = U + PV = 3739 + 0.025 \times 10^5 = 6239 \text{ J}$$

$$(0.8) \quad F = U - TS = 3739 - 298 \times 155 = -4.2 \times 10^4 \text{ J}$$

$$(0.9) \quad G = F + PV = -4.2 \times 10^4 + 0.025 \times 10^5 = -4 \times 10^4 \text{ J}$$

Since in practice, only differences in energy are measured, the fact that  $F$  and  $G$  are negative shouldn't worry us.

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