

## 5.1 Free Energy as Available Work

In Section 1.6 I defined the **enthalpy** of a system as its energy plus the work needed to make room for it, in an environment with constant pressure  $P$ :

$$H \equiv U + PV. \quad (5.1)$$

This is the total energy you would need, to create the system out of nothing and put it in such an environment. (Since the initial volume of the system is zero,  $\Delta V = V$ .) Or, if you could completely annihilate the system,  $H$  is the energy you could recover: the system's energy plus the work done by the collapsing atmosphere.

Often, however, we're not interested in the total energy needed or the total energy that can be recovered. If the environment is one of constant temperature, the system can extract heat from this environment for free, so all *we* need to provide, to create the system from nothing, is any additional *work* needed. And if we annihilate the system, we generally can't recover all its energy as work, because we have to dispose of its entropy by dumping some heat into the environment.

So I'd like to introduce two more useful quantities that are related to energy and analogous to  $H$ . One is the **Helmholtz free energy**,

$$F \equiv U - TS. \quad (5.2)$$

This is the total energy needed to create the system, minus the heat you can get for free from an environment at temperature  $T$ . This heat is given by  $T\Delta S = TS$ , where  $S$  is the system's (final) entropy; the more entropy a system has, the more of its energy can enter as heat. Thus  $F$  is the energy that must be provided as work, if you're creating the system out of nothing.\* Or if you annihilate the system, the energy that comes out as work is  $F$ , since you have to dump some heat, equal to  $TS$ , into the environment in order to get rid of the system's entropy. The *available*, or "free," energy is  $F$ .

The word "work" in the previous paragraph means *all* work, including any that is done automatically by the system's surroundings. If the system is in an environment with constant pressure  $P$  and constant temperature  $T$ , then the work *you* need to do to create it, or the work you can recover when you destroy it, is given by the **Gibbs free energy**,

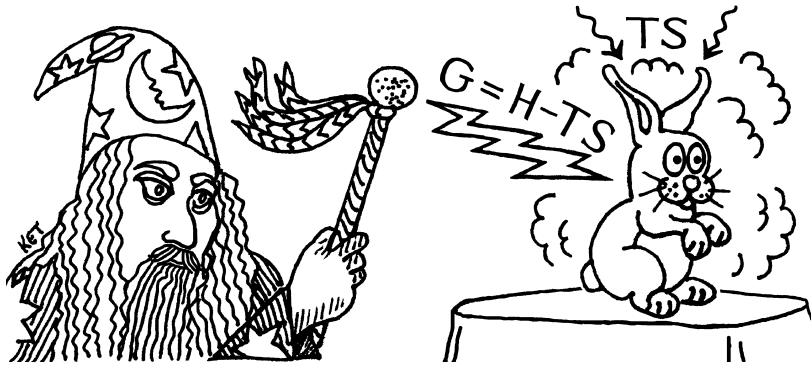
$$G \equiv U - TS + PV. \quad (5.3)$$

This is just the system's energy, minus the heat term that's in  $F$ , plus the atmospheric work term that's in  $H$  (see Figure 5.1).

[This section continues to discuss changes in  $F$  and  $G$ ...]

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\*In the context of creating a system, the term *free* energy is a misnomer. The energy that comes for free is  $TS$ , the term we *subtracted* to get  $F$ . In this context,  $F$  should be called the *costly* energy. The people who named  $F$  were instead thinking of the reverse process, where you annihilate the system and recover  $F$  as work.



**Figure 5.1.** To create a rabbit out of nothing and place it on the table, the magician need not summon up the entire enthalpy,  $H = U + PV$ . Some energy, equal to  $TS$ , can flow in spontaneously as heat; the magician must provide only the difference,  $G = H - TS$ , as work. (Illustration by Karen Thurber.)