

9.13: Defining the Helmholtz and Gibbs Free Energies

The first and second laws of thermodynamics define energy and entropy. Energy and entropy are fundamental state functions that we use to define other state functions. In Chapter 8, we use the energy function to define enthalpy. We use the energy and entropy functions to define two more state functions that also prove to have useful properties. These are the Helmholtz and Gibbs free energies. The **Helmholtz free energy** is usually given the symbol A , and the **Gibbs free energy** is usually given the symbol G . We define them by

$$A = E - TS \quad (\text{Helmholtz free energy})$$

and

$$G = H - TS \quad (\text{Gibbs free energy})$$

Note that PV , TS , H , A , and G all have the units of energy, E .

The sense of the name “free energy” is that a constant-temperature process in which a system experiences an entropy increase ($\Delta S > 0$) is one in which the system’s ability to do work in the surroundings is increased by an energy increment $T\Delta S$. Then, adding $T\Delta S$ to the internal energy lost by the system yields the amount of energy that the process actually has available (energy that is “free”) to do work in the surroundings. When we consider how ΔA and ΔG depend on the conditions under which system changes, we find that this idea leads to useful results.

The rest of this chapter develops important equations for ΔE , ΔH , ΔS , ΔA , and ΔG that result when we require that a system change occur under particular sets of conditions.

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