9.17: Notation and Terminology- Conventions for Spontaneous Processes

We now want to consider criteria for a spontaneous process in which a closed system passes from state A to state B. State B can be an equilibrium state, but state A is not. We can denote the energy change for this process as $\Delta_{AB}E$, and we can find it by measuring the heat and work exchanged with the surroundings as the process takes place, $\Delta_{AB}E = q + w$, or for a process in which the increments of heat and work are arbitrarily small, $d_{AB}E = dq + dw$. Likewise, we can denote the entropy change for the spontaneous process as $\Delta_{AB}S$ or $d_{AB}S$, but we cannot find the entropy change by measuring q^{spon} or dq^{spon}. If we cannot find the entropy change, we cannot find the Helmholtz or Gibbs free energy changes from their defining relationships, $A = E - TS$ and $G = H - TS$. Moreover, intensive variables—pressure, temperature, and concentrations—may not have well-defined values in a spontaneously changing system.

When we say that a reversible process occurs with some thermodynamic variable held constant, we mean what we say: The thermodynamic variable has the same value at every point along the path of reversible change. In the remainder of this chapter, we develop criteria for spontaneous change. These criteria are statements about the values of ΔE, ΔH, ΔA, and ΔG for a system that can undergo spontaneous change under particular conditions. In stating some of these criteria, we specify the conditions by saying that the pressure or the temperature is constant. As we develop these criteria, we will see that these stipulations have specific meanings. When we say that a process occurs “at constant volume” (isochorically), we mean that the volume of the system remains the same throughout the process. When we say that a spontaneous process occurs “at constant pressure” (isobarically or isopiestically), we mean that the pressure applied to the system by the surroundings is constant throughout the spontaneous process and that the system pressure is equal to the applied pressure, $P = P_{applied}$, at all times. When we say that a spontaneous process occurs “at constant temperature”, we may mean only that

1. the system is continuously in thermal contact with its surroundings
2. the temperature of the surroundings is constant
3. in the initial and final states, the system temperature is equal to the surroundings temperature.