9.18: The Heat Exchanged by A Spontaneous Process at Constant Entropy

To continue our effort to find change criteria that use only properties of the system, let us consider a spontaneous process, during which the system is in contact with its surroundings and the entropy of the system is constant. For every incremental part of this process, we have $dS = 0$ and $dS + d\hat{S} > 0$. Hence, $d\hat{S} > 0$. It follows that $\Delta S = 0$, $\Delta S + \Delta \hat{S} > 0$, and $\Delta \hat{S} > 0$. (Earlier, we found that the entropy changes for a spontaneous process in an isolated system are $\Delta S > 0$ and $\Delta \hat{S} = 0$. The present system is not isolated.) Since the change that occurs in the system is irreversible, $dS = 0$ does not mean that $dq = 0$. The requirement that $dS = 0$ places no constraints on the temperature of the system or of the surroundings at any time before, during, or after the process occurs.

In Section 9.15, we find $dS > dq^{spon}/\hat{T}$ for any spontaneous process in a closed system. If the entropy of the system is constant, we have

$$dq^{spon} < 0$$

(spontaneous process, constant entropy)

for every incremental part of the process. For any finite change, it follows that the overall heat must satisfy the same inequality:

$$q^{spon} < 0$$

(spontaneous process, constant entropy)

For a spontaneous process that occurs with the system in contact with its surroundings, but in which the entropy of the system is constant, the system must give up heat to the surroundings. $dq < 0$ and $q < 0$ are criteria for spontaneous change at constant system entropy.

In Section 9.14, we develop criteria for reversible processes. The criteria relate changes in the system's state functions to the reversible non-pressure–volume work that is done on the system during the process. Now we can develop parallel criteria for spontaneous processes.