Entropy Change in Calorimetric Processes

A substance of mass \( m_1 \), specific heat \( c_1 \), and initial temperature \( T_1 \) is placed in thermal contact with a second substance of mass \( m_2 \), specific heat \( c_2 \), and initial temperature \( T_2 > T_1 \). The two substances are contained in a calorimeter so that no energy is lost to the surroundings. The system of the two substances is allowed to reach thermal equilibrium. What is the total entropy change for the system?

First, let us calculate the final equilibrium temperature \( T_f \). Using the techniques of Section 20.2,—namely, Equation 20.5, \( Q_{\text{cold}} = -Q_{\text{hot}} \), and Equation 20.4, \( Q = mc \Delta T \), we obtain

\[
m_1 c_1 \Delta T_1 = -m_2 c_2 \Delta T_2
\]

\[
m_1 c_1 (T_f - T_1) = -m_2 c_2 (T_f - T_2)
\]

Solving for \( T_f \), we have

\[
T_f = \frac{m_1 c_1 T_1 + m_2 c_2 T_2}{m_1 c_1 + m_2 c_2}
\]  

(22.14)

The process is irreversible because the system goes through a series of non-equilibrium states. During such a transformation, the temperature of the system at any time is not well defined because different parts of the system have different temperatures. However, we can imagine that the hot substance at the initial temperature \( T_2 \) is slowly cooled to the temperature \( T_f \) as it comes into contact with a series of reservoirs differing infinitesimally in temperature, the first reservoir being at \( T_2 \) and the last being at \( T_f \). Such a series of very small changes in temperature would approximate a reversible process. We imagine doing the same thing for the cold substance. Applying Equation 22.9 and noting that \( dQ = mc \, dT \) for an infinitesimal change, we have

\[
\Delta S = \int_1^2 \frac{dQ_{\text{cold}}}{T} + \int_1^2 \frac{dQ_{\text{hot}}}{T} = m_1 c_1 \int_{T_1}^{T_f} \frac{dT}{T} + m_2 c_2 \int_{T_2}^{T_f} \frac{dT}{T}
\]

where we have assumed that the specific heats remain constant. Integrating, we find that

\[
\Delta S = m_1 c_1 \ln \frac{T_f}{T_1} + m_2 c_2 \ln \frac{T_f}{T_2}
\]

(22.15)

where \( T_f \) is given by Equation 22.14. If Equation 22.14 is substituted into Equation 22.15, we can show that one of the terms in Equation 22.15 is always positive and the other is always negative. (You may want to verify this for yourself.) The positive term is always greater than the negative term, and this results in a positive value for \( \Delta S \). Thus, we conclude that the entropy of the Universe increases in this irreversible process.

Finally, you should note that Equation 22.15 is valid only when no mixing of different substances occurs, because a further entropy increase is associated with the increase in disorder during the mixing. If the substances are liquids or gases and mixing occurs, the result applies only if the two fluids are identical, as in the following example.

**Example 22.9  Calculating \( \Delta S \) for a Calorimetric Process**

Suppose that 1.00 kg of water at 0.00°C is mixed with an equal mass of water at 100°C. After equilibrium is reached, the mixture has a uniform temperature of 50.0°C. What is the change in entropy of the system?

\[
\Delta S = m_1 c_1 \ln \frac{T_f}{T_1} + m_2 c_2 \ln \frac{T_f}{T_2}
\]

\[
= (1.00 \text{ kg})(4,186 \text{ J/kg·K}) \ln \left( \frac{323 \text{ K}}{273 \text{ K}} \right)
\]

\[
+ (1.00 \text{ kg})(4,186 \text{ J/kg·K}) \ln \left( \frac{323 \text{ K}}{373 \text{ K}} \right)
\]

\[
= 704 \text{ J/K} - 602 \text{ J/K} = 102 \text{ J/K}
\]

That is, as a result of this irreversible process, the increase in entropy of the cold water is greater than the decrease in entropy of the warm water. Consequently, the increase in entropy of the system is 102 J/K.