20.9: The Statistical Definition of Entropy is Analogous to the Thermodynamic Definition

We learned earlier in 20-5 that entropy, S, is related to the number of microstates, W, in an ensemble with A systems:

$$S_{ensemble} = k_B \ln W \tag{20.9.1}$$

and

$$W = \frac{A!}{\prod_j a_j!} \tag{20.9.2}$$

Combining Equations 20.9.1 and 20.9.2 to get:

$$\begin{aligned} S_{ensemble} &= k_B \ln \frac{A!}{\prod_j a_j!} \\ &= k_B \ln A! - k_B \sum_j \ln a_j! \end{aligned}$$

Using Sterling's approximation:

$$\ln A! \approx A \ln A - A$$

We obtain:

$$S_{ensemble} = k_B A \ln A - k_B A - k_B \sum_j a_j \ln a_j + k_B \sum a_j$$

Since:

$$A = \sum a_j$$

The expression simplifies to:

$$S_{ensemble} = k_B A \ln A - k_B \sum_j a_j \ln a_j$$

We can make use of the fact that the number of microstates in state j is equal to the total number of microstates multiplied by the probability of finding the system in state j, p_j:

$$a_j = p_j A$$

Plugging in, we obtain

$$\begin{aligned} S_{ensemble} &= k_B A \ln A - k_B \sum_j p_j A \ln p_j A \\ &= k_B A \ln A - k_B \sum_j p_j A \ln p_j - k_B \sum_j p_j A \ln A \end{aligned}$$

Since A is a constant and the sum of the probabilities of finding the system in state j is always 1:

$$\sum p_j = 1$$

The first and last term cancel out:

$$S_{ensemble} = -k_B A \sum_j p_j \ln p_j$$

We can use that the entropy of the system is the entropy of the ensemble divided by the number of systems:

$$S_{system} = S_{ensemble} / A$$

Dividing by A, we obtain:

$$S_{system} = -k_B \sum_j p_j \ln p_j$$

We can differentiate this equation and dropping the subscript:

$$dS = -k_B \sum_j (dp_j + \ln p_j dp_j)$$

Since $\sum_j p_j = 1$, the derivative $\sum_j dp_j = 0$:

$$dS = -k_B \sum_j \ln p_j dp_j$$

In short:

$$\sum_j \ln p_j dp_j = -\frac{\delta q_{rev}}{k_B T}$$

Plugging in:

$$dS = \frac{\delta q_{rev}}{T}$$
