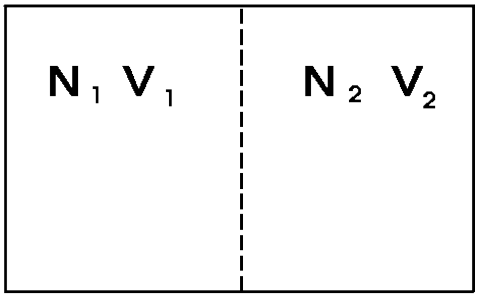
Answer on Question #61172-Physics-Molecular Physics | Thermodynamics

What is a Gibbs paradox? How did it arise?

Answer

Consider an ideal gas of *N* particles in a container with a volume *V*. A partition separates the container into two sections with volumes V_1 and V_2 , respectively, such that $V_2 + V_2 = V$. Also, there are N_1 particles in the volume V_1 and N_2 particles in the volume V_2 . It is assumed that the number density is the same throughout the system

$$\rho = \frac{N_1}{V_1} = \frac{N_2}{V_2}$$



$$N_1 + N_2 = N$$

$$V_1 + V_2 = V$$

If the partition is now removed, what should happen to the total entropy? Since the particles are identical, the total entropy should not increase as the partition is removed because the two states cannot be differentiated due to the indistinguishability of the particles. Let us analyze this thought experiment using the classical expression entropy derived above (i.e., we leave off the $\ln N!$ term).

The entropies S_1 and S_2 before the partition is removed are

$$S_1 \sim N_1 k \ln V_1 + \frac{3}{2} N_1 k$$
$$S_2 \sim N_2 k \ln V_2 + \frac{3}{2} N_2 k$$

And the total entropy is

$$S = S_1 + S_2$$

After the partition is removed, the total entropy is

$$S \sim (N_1 + N_2) k \ln(V_1 + V_2) + \frac{3}{2}(N_1 + N_2) k$$

Thus, the difference

$$\Delta S = S_{\text{after}} - S_{\text{before}}$$

$$\begin{aligned}\Delta S &= (N_1 + N_2) k \ln(V_1 + V_2) - N_1 k \ln V_1 - N_2 k \ln V_2 \\ &= N_1 k \ln(V/V_1) + N_2 k \ln(V/V_2) > 0\end{aligned}$$

This contradicts our predicted result that $\Delta S = 0$. Therefore, the classical expression must not be quite right.

Let us now restore the $\ln N!$. Using the Stirling approximation

$$\ln N! = N \ln N - N$$

the entropy can be written as

$$S = Nk \left[\frac{V}{Nh^3} \left(\frac{2\pi m}{\beta} \right)^{3/2} \right] + \frac{5}{2} Nk$$

which is known as the *Sackur-Tetrode* equation. Using this expression for the entropy, the difference now becomes

$$\begin{aligned} \Delta S &= (N_1 + N_2) k \ln \left(\frac{V_1 + V_2}{N_1 + N_2} \right) - N_1 k \ln(V_1/N_1) - N_2 k \ln(V_2/N_2) \\ &= N_1 k \ln(V/V_1) + N_2 k \ln(V/V_2) - N_1 k \ln(N/N_1) - N_2 k \ln(N/N_2) \\ &= N_1 k \ln \left(\frac{V}{N} \frac{N_1}{V_1} \right) + N_2 k \ln \left(\frac{V}{N} \frac{N_2}{V_2} \right) \end{aligned}$$

However, since the density

$$\rho = N_1/V_1 = N_2/V_2 = N/V$$

is constant, the terms appearing in the log are all 1 and, therefore, vanish. Hence, the change in entropy, $\Delta S = 0$ as expected. Thus, it seems that the $1/N!$ term is absolutely necessary to resolve the paradox. This means that only a correct quantum mechanical treatment of the ideal gas gives rise to a consistent entropy.