

2.14: Effective Equivalence of the Isothermal and Constant-energy Conditions

In principle, an isolated system is different from a system with identical macroscopic properties that is in equilibrium with its surroundings. We emphasize this point, because this distinction is important in the logic of our development. However, our development also depends on the assumption that, when N is a number that approximates the number molecules in a macroscopic system, the constant-temperature and constant-energy systems are functionally equivalent.

In [Section 20.9](#), we find that any calculation of macroscopic properties must produce the same result whether we consider the constant-temperature or the constant-energy system. The most probable population set, $\{N_1^*, N_2^*, \dots, N_i^*, \dots\}$, provides an adequate description of the macroscopic state of the constant-temperature system precisely because it is representative of all the population sets that contribute significantly to the total probability of the constant-temperature system. The effective equivalence of the constant-temperature and constant-energy systems ensures that the most probable population set is also representative of all the population sets that contribute significantly to the total probability of the constant-energy system.

In [Section 20.12](#), we see that the essential equivalence of the isothermal and constant-energy systems means that we have

$$1 = \Omega_E \prod_{i=1}^{\infty} \rho(\epsilon_i)^{N_i^*}$$

Taking logarithms of both sides, we find

$$\ln \Omega_E = - \sum_{i=1}^{\infty} N_i^* \ln \rho(\epsilon_i)$$

From $S = k \ln \Omega_E$, it follows that

$$S = -k \sum_{i=1}^{\infty} N_i^* \ln \rho(\epsilon_i)$$

For the constant-temperature system, we have $N_i^* = N P_i$. When we assume that the equilibrium constant-temperature and constant-energy systems are essentially equivalent, the entropy of the N -molecule system becomes

$$\begin{aligned} S &= -k \sum_{i=1}^{\infty} N_i^* \ln \rho(\epsilon_i) \\ &= -kN \sum_{i=1}^{\infty} P_i \ln \rho(\epsilon_i) \end{aligned}$$

so that we obtain the same result from assuming that $S = k \ln \Omega_E$ as we do in [Section 20.10](#) from assuming that $S = k \ln W_{max}$. Under the approximations we introduce, $\ln \Omega_E$ and $\ln W_{max}$ evaluate to the same thing.

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