Chem. Educator **1999,** *4,* 211–213

Simple Statistical Calculations of Entropy Changes

Albert Lötz

Institut für Physikalische Chemie, Universität München, Butenandtstr. 11, 81377 Munich, Germany, aloetz@olymp.cup.uni-muenchen.de

Abstract: The simple statistical treatment of the temperature equilibration of two two-level systems provides an easily understandable example of changes in entropy during reversible and irreversible processes. This treatment yields the fundamental formula $dS = dq_{\mathrm{rev}}/T$; thus, it provides a useful link between the classical (macroscopic) and statistical (microscopic) view of thermodynamic processes.

Introduction

Classical thermodynamics treats matter as a continuum. This does not provide a simple picture of what is behind concepts such as internal energy and entropy on a molecular level. Authors of introductory textbooks, therefore, invariably add a microscopic picture of thermodynamic processes to this classical, macroscopic treatment, but only a few textbooks [for instance; 1, 2] present a thorough statistical treatment in close connection with classical thermodynamics. This is because the quantitative treatment of thermodynamics from a molecular point of view demands the knowledge of quantum mechanics and statistical mechanics. Textbook authors usually confine the link to statistical mechanics to the simple example of the entropy change during the isothermal expansion of an ideal gas.

Isothermal Gas Expansion

Most textbooks [for instance, 3–6] either construct a loose connection between entropy and probability, or they present Boltzmann's formula

$$S = k \ln W \tag{1}$$

Some authors use the common definition ($0 \le W \le 1$) of probability, W, in this context instead of the correct thermodynamic definition ($W \ge 1$). This may be partially justified because of the sketchy reasoning within the context. Nevertheless, it can be presented more correctly, and with little additional expense, by writing the thermodynamic probability as the number of ways of distributing N_{A} (Avogadro's number) gas molecules among Z cells of molecular dimensions and volume, v, into which the total gas volume, V, is imagined to be divided.

$$W = \binom{Z}{N_{\mathrm{A}}} = \frac{Z(Z-1)\ldots(Z-(N_{\mathrm{A}}-1))}{N_{\mathrm{A}}!} \tag{2}$$

Because for an ideal gas Z is very large compared to N_{A}, all factors up to $N_{\mathrm{A}} - 1$ can be neglected in the numerator so that

$$W = \binom{Z}{N_{\mathrm{A}}} \approx \frac{Z^{N_{\mathrm{A}}}}{N_{\mathrm{A}}!} = \frac{(V/v)^{N_{\mathrm{A}}}}{N_{\mathrm{A}}!} \tag{3}$$

Thus, the entropy change for the isothermal volume change is

$$\Delta S = k \ln \frac{W_2}{W_1} = k \ln \frac{(V_2/v)^{N_{\mathrm{A}}}/N_{\mathrm{A}}!}{(V_1/v)^{N_{\mathrm{A}}}/N_{\mathrm{A}}!} = R \ln \frac{V_2}{V_1} \tag{4}$$

Temperature Change at Constant Volume

There is a similar logarithmic dependence of the entropy on temperature

$$\Delta S = C_V \ln \frac{T_2}{T_1} \tag{5}$$

This is harder to show on a statistical basis, but it is more interesting, because it involves heat or energy transfer and yields the fundamental formula

$$dS = \frac{dq_{\mathrm{rev}}}{T} \tag{6}$$

when calculated statistically. A simple special case of the statistical calculation, which is easy to understand and clearly shows important features of entropy changes during reversible and irreversible changes (often confusing to students), is demonstrated here. Knowledge of Boltzmann's distribution law and the quantization of energy is assumed.

We consider two two-level systems at two different temperatures that approach one common temperature by thermal contact (see Figure 1). The entropy change for the process in the initially colder system (subscript c) is given by

$$\begin{aligned}\Delta S_{\mathrm{c}} &= k(\ln W_2 - \ln W_1) = k\left(\ln\frac{(m+n)!}{m!n!} - \ln\frac{(m+n)!}{(m+p)!(n-p)!}\right) \\ &= k \ln \frac{(m+p)!(n-p)!}{m!n!}\end{aligned} \tag{7}$$

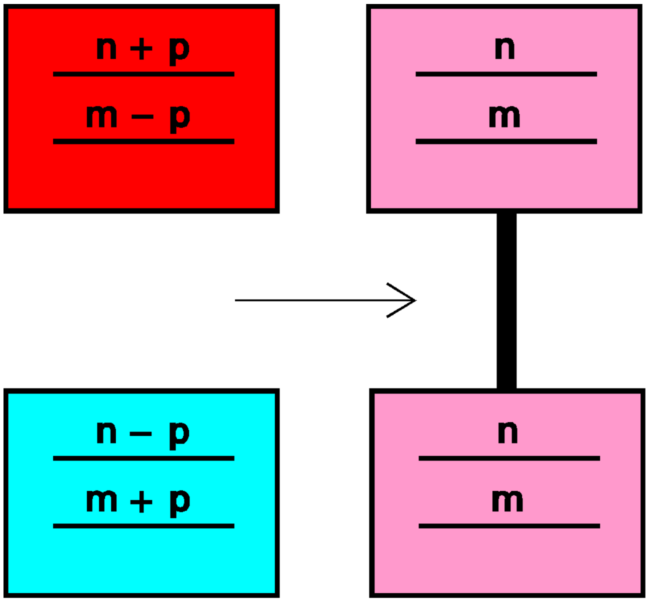

Figure 1. Temperature equilibration of two two-level systems. The upper (warmer) system and the lower (colder) system (left side of figure) reach a common temperature after thermal contact (right side of figure). The letters n, m, and p represent integers and designate the level populations that define the temperatures by Boltzmann's distribution law.

If the initially warmer system is considered, the sign of *p* is reversed in equation 7. We now distinguish two cases, reversible and irreversible.

The reversible case is characterized by quasi-equilibrium, which means the temperatures of the two systems are virtually identical. They are, therefore, represented by the common letter, *T*, in the following. The population deviation from thermal equilibrium, *p*, is much smaller than *n* and *m*; we assume 1 for simplicity. Then, for the initially colder system

$$\Delta S_{\text{c,rev}} = k \ln \frac{(m+1)!(n-1)!}{m!n!} = k \ln \frac{m+1}{n} \approx k \ln \frac{m}{n} \qquad (8)$$

The ratio of the populations *m* and *n* of the two levels can be expressed by Boltzmann's equation

$$\Delta S_{\text{c,rev}} = k \ln e^{(\varepsilon_n - \varepsilon_m)/kT} = \frac{\varepsilon_n - \varepsilon_m}{T} = \frac{q}{T} \qquad (9)$$

The last equality expresses the fact that the energy transfer between the two systems is by heat flow and corresponds to the energy of one particle changing levels in each of the two systems.

The entropy change of the initially warmer system is given by

$$\begin{aligned} \Delta S_{\text{w,rev}} &= k \ln \frac{(m-1)!(n+1)!}{m!n!} \approx k \ln \frac{n}{m} \\ &= k \ln e^{-(\varepsilon_n - \varepsilon_m)/kT} = -\frac{q}{T} \end{aligned} \qquad (10)$$

Thus, the total entropy change for the reversible process is zero

$$\Delta S_{\text{total,rev}} = \Delta S_{\text{c,rev}} + \Delta S_{\text{w,rev}} = 0 \qquad (11)$$

For the irreversible case the total entropy change is

$$\Delta S_{\text{total, irr}} = k \ln \frac{(m+p)!(n-p)!}{m!n!} + k \ln \frac{(m-p)!(n+p)!}{m!n!} \qquad (12)$$

Rearrangement gives

$$\begin{aligned} \Delta S_{\text{total, irr}} &= k \ln \frac{(m+p)!(m-p)!}{m!m!} + k \ln \frac{(n+p)!(n-p)!}{n!n!} \\ &= k \ln \prod_{i=1}^{p} \frac{m+i}{m-p+i} + k \ln \prod_{i=1}^{p} \frac{n+i}{n-p+i} \end{aligned} \qquad (13)$$

Each factor of the two products is larger than 1, which means that the total entropy change of the irreversible heat transfer is positive

$$\Delta S_{\text{total,irr}} > 0 \qquad (14)$$

Another irreversible case that can be demonstrated is the infinitesimal heat transfer from a warm system at temperature T_{w} to a cold system at temperature T_{c} in which the populations of all levels change by only one unit ($\Delta p = \pm 1$). The entropy change for the infinitesimal cooling of the warm system is given by

$$\begin{aligned} \Delta S_{\text{w}} &= k \left(\ln \frac{(m+n)!}{(m-p+1)!(n+p-1)!} - \ln \frac{(m+n)!}{(m-p)!(n+p)!} \right) \\ &= k \ln \frac{n+p}{m-p+1} \approx k \ln \frac{n+p}{m-p} = -\frac{q}{T_{\text{w}}} \end{aligned} \qquad (15)$$

The corresponding expression for the infinitesimal warming of the cold system is

$$\begin{aligned} \Delta S_{\text{c}} &= k \left(\ln \frac{(m+n)!}{(m+p-1)!(n-p+1)!} - \ln \frac{(m+n)!}{(m+p)!(n-p)!} \right) \\ &\approx k \ln \frac{m+p}{n-p} = \frac{q}{T_{\text{c}}} \end{aligned} \qquad (16)$$

Thus, the total entropy change in the process is

$$\Delta S_{\text{total,irr}} = \Delta S_{\text{c}} + \Delta S_{\text{w}} = \frac{q}{T_{\text{c}}} - \frac{q}{T_{\text{w}}} > 0 \quad (T_{\text{w}} > T_{\text{c}}) \qquad (17)$$

Conclusions

The simple statistical calculations described above yield results for the reversible or irreversible entropy changes in a thermodynamic process. They show that the total entropy change of a closed system is zero during the reversible process and positive during the irreversible process. The reversible process is mathematically shown to be a limiting case of the irreversible process, even for heat flow from a warmer to a colder body, commonly regarded as a typically irreversible process. The fundamental formula $dS = dq_{\text{rev}}/T$ is shown to be valid for heat flow in the reversible case; whereas, it does not apply during an irreversible heat flow. The appearance of the formula $dS = dq_{rev}/T$ in the description of the entropy changes in an infinitesimal and irreversible heat flow from a warmer to a colder system points to the reversible path along which the same change can take place. It includes a third system with which heat is reversibly exchanged at the two temperatures in separate contacts. The temperature change of the third system between the contacts may take place isentropically, for instance, by adiabatic expansion and compression. Although no general validity of the above statements can be derived from the example calculated statistically, the treatment provides detailed insight into the process and helps students to understand the meaning of the general laws that are demonstrated here for a special case.

References

1. Barrow, G. M. *Physical Chemistry*; McGraw-Hill: New York, 1996; p 192.
2. Berry, R. S.; Rice, S. A.; Ross, J. *Physical Chemisty*; Wiley: New York, 1980; p 581.
3. Atkins, P. W. *Physical Chemistry*; Oxford University Press: Oxford, 1994; p 129.
4. Ladd, M. F. *Introduction to Physical Chemistry*; Cambridge University Press: Cambridge, 1998; p 185.
5. Levine, I. N. *Physical Chemistry*; McGraw-Hill: New York, 1995; p 93.
6. Mortimer, R. G. *Physical Chemistry*, Benjamin/Cummings: Redwood City, 1993; p 121.