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2010 Eur. J. Phys. 31 267

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Entropy generation in a chemical reaction

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Received 14 September 2009, in final form 10 November 2009

Published 29 December 2009

Online at stacks.iop.org/EJP/31/267

Abstract

Entropy generation in a chemical reaction is analysed without using the general formalism of non-equilibrium thermodynamics at a level adequate for advanced undergraduates. In a first approach to the problem, the phenomenological kinetic equation of an elementary first-order reaction is used to show that entropy production is always positive. A second approach assumes that the reaction is near equilibrium to prove that the entropy generation is always greater than zero, without any reference to the kinetics of the reaction. Finally, it is shown that entropy generation is related to fluctuations in the number of particles at equilibrium, i.e. it is associated with a microscopic process.

1. Introduction

Teaching some topics of non-equilibrium thermodynamics to undergraduates is not an easy task. The usual thermodynamics courses for science students emphasize systems at equilibrium [1] and do not pay attention to entropy generation in common phenomena such as heat conduction or a chemical reaction. Moreover, the textbooks that deal with non-equilibrium thermodynamics (see for example [1, 2]) introduce the usual formalism in terms of generalized fluxes and forces before studying those phenomena. A teacher may be interested in explaining some non-equilibrium concepts without using that formalism. The heat conduction problem has been analysed in that way [3]. In this paper entropy generation in a chemical reaction is studied without mentioning the general formalism. The author teaches a thermodynamics course for physics and chemistry students following the well-known textbook by Atkins [4]. Additionally a short introduction to chemical kinetics is given, and at this point the entropy generation in a chemical reaction is explained in simple terms. For those students familiar with the statistical description of matter (or those especially enthusiastic), entropy generation is related to fluctuations in the number of particles at equilibrium, i.e. it is related to microscopic properties of the system.

Consequently, the aim of this paper is twofold.

- (1) To evaluate the entropy production in a chemical reaction without mentioning the general formalism of non-equilibrium thermodynamics.
- (2) To show that entropy production is related at a microscopic level with fluctuations in the number of particles.

It may be used in two ways.

- (1) To close a thermodynamics course with an introduction to chemical kinetics.
- (2) To show the relationship between microscopic and macroscopic properties in a statistical mechanics course that includes processes out of equilibrium.

2. Macroscopic analysis

A chemical reaction is described by $\nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D$. The ν_i are the stoichiometric coefficients that are positive for the products (C and D) and negative for the reactants (A and B). The starting point of the analysis is the Gibbs equation:

$$dU = T dS - P dV + \sum_i \mu_i dn_i. \quad (1)$$

As usual U , T , S , P , V , μ_i and n_i are the internal energy, temperature, entropy, pressure, volume, chemical potential and number of moles of i . The first principle states that $dU = dQ + dW$, where dQ is the energy transferred as heat to the system and dW the work done on a system; assuming that there is only expansion work, i.e. $dW = -p dV$, equation (1) can be written as

$$dS = \frac{1}{T} dQ - \frac{1}{T} \sum_i \mu_i dn_i. \quad (2)$$

It should be remembered that the extent of reaction ξ is related to the number of moles n_i and of particles N_i by

$$\begin{aligned} \nu_i d\xi &= dn_i, \\ &= \frac{1}{N_{AV}} dN_i, \\ &= \frac{k_B}{R} dN_i. \end{aligned} \quad (3)$$

As usual, N_{AV} is the Avogadro constant, R is the gas constant and k_B is the Boltzmann constant.

Introducing the time differential dt in (2) and calling $\dot{Q} = dQ/dt$ one gets

$$\frac{dS}{dt} = \frac{\dot{Q}}{T} - \frac{1}{T} \sum_i \nu_i \mu_i \frac{d\xi}{dt}. \quad (4)$$

The first term in (4) is the entropy production per unit time due to the heat exchange with the surroundings while the second term is the entropy generation associated with the chemical reaction itself.

The affinity of a chemical reaction is

$$\mathcal{A} = - \sum_i \nu_i \mu_i. \quad (5)$$

It is zero at equilibrium because the chemical potentials of reactants and products are equal. A positive value of the affinity means that the chemical potentials of the reactants are greater than those of the products, and the reaction still goes forward.

If S_{ext} is the entropy generated due to the interaction with the surroundings and S_{int} is that generated inside the system, one may rewrite (4) as

$$\frac{dS}{dt} = \dot{S}_{\text{ext}} + \dot{S}_{\text{int}}. \quad (6a)$$

Because the entropy production rate \dot{S}_{ext} due to the interactions with the surrounding is

$$\dot{S}_{\text{ext}} = \dot{Q}/T, \quad (6b)$$

and using definition (5), it follows that the production rate of entropy \dot{S}_{int} inside the system is

$$\dot{S}_{\text{int}} = \frac{\mathcal{A}}{T} \frac{d\xi}{dt}. \quad (6c)$$

Equations (6) are a central result; they show how the entropy changes in the system and clearly distinguish the contribution of the chemical reaction itself. A simple example clarifies this point.

An elementary first-order reaction is considered: $A \rightarrow B$, and the reaction velocity w is given by $w = kn_A$, where k is a phenomenological constant greater than zero. Although in chemical kinetics the reaction velocity is defined in terms of concentrations, in this paper it is assumed that the volume remains constant and the velocity is written in terms of the number of moles:

$$\begin{aligned} w &= \frac{1}{v_A} \frac{dn_A}{dt}, \\ &= \frac{d\xi}{dt}, \\ &= kn_A. \end{aligned} \quad (7)$$

From (6c) and (7) one gets

$$\dot{S}_{\text{int}} = kn_A \frac{\mathcal{A}}{T} \geq 0. \quad (8)$$

This result shows that the entropy production due to the reaction is always positive as demanded by the second principle (remember that $\mathcal{A} > 0$ if the system is not yet in equilibrium). A similar calculation could be carried out for reactions of higher order, but the conclusion is the same.

It has been shown that the entropy production in a system where a chemical reaction takes place can be written as the sum of two contributions (equations (6)). For this particular example—a first-order elementary reaction—it is explicitly shown that entropy is always generated by the reaction itself. This conclusion is reached by using thermodynamical considerations and a phenomenological constant, i.e. this is a purely macroscopic result. An alternative approach, without any reference to the kinetics, is given in the next section.

3. A more detailed analysis

The aim of this section is to introduce chemical potential in the analysis of the entropy generation and to find an expression for it without reference to the kinetics.

The chemical potential of an ideal solution can be written in different ways [5]. A convenient one is

$$\mu_i = \mu_i^\theta(T, p) + RT \ln \left(\frac{c_i}{c^\theta} \right). \quad (9)$$

In this equation c_i is the concentration expressed as the number of moles n_i per unit mass.

The chemical potential always refers to a standard state designated with the symbol θ . Remembering the relations between the mole n_i and the number of particles N_i , (9) can be written as

$$\begin{aligned}\mu_i &= \eta'(T, p) + RT \ln n_i, \\ &= \eta(T, p) + RT \ln N_i.\end{aligned}\quad (10)$$

η' and η are functions that do not depend on the concentration of the chemical species i .

To express the chemical potential in terms of the number of particles is usual in statistical mechanics textbooks for physics undergraduates [6, 7]. Therefore, the second line of equation (10) is familiar to physics students while those in chemistry would prefer to start the analysis from equation (9).

The symbol ' eq ' is used to designate a physical magnitude in equilibrium; since the affinity is zero in equilibrium, one can write

$$\begin{aligned}\mathcal{A} &= - \sum_i v_i \mu_i + \sum_i v_i \mu_i^{eq}, \\ &= -RT \sum_i v_i \ln \left(\frac{N_i}{N_i^{eq}} \right).\end{aligned}\quad (11)$$

The next step evaluates the entropy generated when the chemical reaction goes from a state characterized by the values N_i^0 and ξ^0 to the equilibrium state with N_i^{eq} and ξ^{eq} . From equations (3), (6a) and (11), we find

$$\begin{aligned}\Delta S_{\text{int}} &= \int \frac{\mathcal{A}}{T} \frac{d\xi}{dt} dt, \\ &= -R \sum_i \int_{\xi^0}^{\xi^{eq}} v_i \ln \left(\frac{N_i}{N_i^{eq}} \right) d\xi, \\ &= -R \sum_i \int_{\xi^0}^{\xi^{eq}} v_i \ln \left(\frac{\xi}{\xi^{eq}} \right) d\xi.\end{aligned}\quad (12)$$

The integral can be evaluated and the result rewritten in terms of the number of particles:

$$\Delta S_{\text{int}}/k_B = - \sum_i \left[(N_i^0 - N_i^{eq}) - N_i \ln \left(\frac{N_i^0}{N_i^{eq}} \right) \right]. \quad (13)$$

Up to this point the results are completely general, but a new assumption has to be made to proceed. It is assumed that the system is close to equilibrium; the right-hand side of (13) can be expanded as a power series and only the most relevant contribution kept. This yields

$$\Delta S_{\text{int}}/k_B = \frac{1}{2} \sum_i \frac{1}{N_i^{eq}} (N_i^0 - N_i^{eq})^2. \quad (14a)$$

This expression may be rewritten in terms of easily measurable quantities:

$$\Delta S_{\text{int}}/R = \frac{1}{2} \sum_i \frac{1}{n_i^{eq}} (n_i^0 - n_i^{eq})^2. \quad (14b)$$

Equation (14b) is preferred by chemistry students because all the quantities on the right-hand side are macroscopic and measurable. However, physics students are more interested in the relation of entropy generation with the microscopic view of matter. For them it is convenient to introduce a parameter λ and rewrite the above expression as

$$\begin{aligned}\lambda &= \sum_i \frac{v_i^2}{n_i^{eq}}, \\ \Delta S_{\text{int}}/R &= \frac{1}{2} \lambda (\xi^0 - \xi^{eq})^2.\end{aligned}\quad (14c)$$

It is obvious that λ is always positive and entropy is always generated by the reaction as required by the second principle. Note that λ is a macroscopic quantity—it can be evaluated just by knowing the stoichiometric coefficients and the equilibrium concentrations—but its microscopic interpretation will come out in the next section.

4. Microscopic analysis

The results given by equations (14) are valid for any reaction close to equilibrium. However, to understand the meaning of λ a simple reaction of the kind $A \rightarrow B$ is analysed.

For this particular reaction, the total number of particles N remains constant: $N = N_A^0 + N_B^0 = N_A^{eq} + N_B^{eq}$.

At a microscopic level an A molecule has two options: it remains as an A molecule with probability p or it becomes a B molecule with probability $(1-p)$. This means that the number of particles follows the well-known binomial distribution. From elementary probabilistic theory [8, 9] it is known that the average numbers of A and B molecules in equilibrium are

$$N_A^{eq} = pN, \quad N_B^{eq} = (1-p)N. \quad (15)$$

For a binomial distribution [8, 9], the variance σ is

$$\sigma^2 = p(1-p)N. \quad (16a)$$

So, for the system described by equation (15), the variance σ_{eq} at equilibrium can be written as

$$\sigma_{eq}^2 = \frac{N_A^{eq} N_B^{eq}}{N}. \quad (16b)$$

Using the expression of N given above, it finally results that

$$\sigma_{eq}^2 = \left(\frac{1}{N_A^{eq}} + \frac{1}{N_B^{eq}} \right)^{-1}. \quad (16c)$$

From equation (14c) and considering that $\nu_A = \nu_B = 1$ for this particular reaction, the value of λ can be evaluated:

$$\begin{aligned} \lambda &= \frac{1}{n_A^{eq}} + \frac{1}{n_B^{eq}} \\ &= \left(\frac{1}{N_A^{eq}} + \frac{1}{N_B^{eq}} \right) N_{AV}. \end{aligned} \quad (17)$$

Comparing it with (16c) one gets

$$\lambda = \frac{N_{AV}}{\sigma_{eq}^2}. \quad (18)$$

Thus, from the second line of equation (14c) it comes out that the total entropy produced by the elementary reaction considered in this section is

$$\Delta S_{\text{int}} = \frac{RN_{AV}}{2} \frac{1}{\sigma_{eq}^2} (\xi^0 - \xi^{eq})^2. \quad (19)$$

Besides a numerical factor, the produced entropy is related to the fluctuations of the number of particles at equilibrium, i.e. the microscopic origin of entropy is clearly shown in (19).

5. Conclusion

The production of entropy in a chemical reaction has been studied at a level adequate to advanced undergraduate students. Starting from the Gibbs relation (equation (1)), it has been shown that the rate of entropy production in a chemical reaction has two contributions: one of them associated with the heat interchanged with the surroundings and the other originated by the reaction itself (equations (6)). For an elementary first-order reaction it has been proved that the entropy produced by the reaction is always positive (equation (8)). To get this result the kinetics of the reaction has to be explicitly known. An alternative approach developed in section 3 gives the total entropy generated by the reaction in terms of macroscopic measurable magnitudes (equation (14b)). Finally, a microscopic analysis of the problem was carried out and it comes out that the entropy production is associated with the fluctuations of the number of particles (equation (19)). Once again statistical physics sheds light on the origin of entropy. Although the calculation was performed for the elementary reaction previously considered, it could be generalized for any reaction; the details, however, become cumbersome and nothing new is learned.

Acknowledgment

The author thanks the National Scientific and Technological Research Council (CONICET) of Argentina for financial support.

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