

The connection between the second law of thermodynamics and the principle of microscopic reversibility

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Abstract The connection between the second law of thermodynamics and the principle of microscopic reversibility is studied with mathematical rigor. It is shown that a kinetic scheme adhering to microscopic reversibility necessarily obeys the second law. In addition, it is also proved that any reaction linearly independent from the others must be microscopically reversible. This condition is not necessary for reactions whose stoichiometry can be given as a linear combination of others. An example is given to prove this fact.

Keywords Microscopic reversibility · Detailed balance · Second law of thermodynamics

1 Introduction

The principle of microscopic reversibility is an important concept in chemical kinetics [1, 2]. A common way to state the principle is to postulate that any molecular process and its reverse occur with equal rates at equilibrium. It is most often used to falsify certain mechanistic possibilities [3–7]. In recent research, the use and consequences of the principle have become very important in models of ion channels [8, 9] and studying the feasibility of recycling in mathematical models of the origin of homochirality [10–12].

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The principle is often viewed as direct consequence of the laws of thermodynamics. However, this has never been proved. For example, Tolman wrote the following in his 1925 paper [1] dealing with the principle:

...the principle of microscopic reversibility can be regarded at the present time only as an unproved assumption. Although closely connected with the second law of thermodynamics, it cannot be derived therefrom. (p. 439, top lines) [1].

Despite these clear remarks, the work of Tolman is often cited in support of the universal validity of the principle with the only generally accepted exception of photochemical reactions [10–12]. This exception is rather odd from a theoretical point view because there is no special second law of thermodynamics for photochemical processes nor there is a special definition of photochemical reaction rate.

After almost a century, the connection between the second law of thermodynamics and the principle of microscopic reversibility has still not been demonstrated. The reason for this may be the fact that classical thermodynamics is based on individual substances as basic units and not chemical reactions. When chemical reactions are chosen for the basis of thermodynamic considerations, significant difficulties arise, which were only solved in a mathematically rigorous manner by the theory of response reactions introduced in the past two decades [13–16].

The present work aims to clarify the connection between the laws of thermodynamics and the principle of microscopic reversibility. Some routine mathematical derivation will be given in the Supporting Information.

2 Results and discussion

Any system of chemical reactions can be represented by the following stoichiometric equations:

$$\sum_{j=1}^N v_{ij} X_j = 0 \quad (i = 1, 2, \dots, M) \quad (1)$$

In Eq. 1, the total number of chemical reactions is M , the total number of substances is N , X_j represents the j th substance, whereas v_{ij} is the stoichiometric coefficient of substance X_j in chemical equation i . The usual conventions will be used: v_{ij} is positive for products, negative for reactants, and zero for substances not appearing in reaction i [17, 18]. The representation in Eq. 1 can obviously be done in a way that the same reaction is not listed twice. The reverse process of all listed reactions will be implied to play some role in all discussion, but this will be done by allowing reaction rates to be negative rather than listing the separate reverse reactions $\sum_{j=1}^N -v_{ij} X_j = 0$. It is a fundamental postulate of kinetics that every chemical process can be given as a series of elementary reactions. For reasons outlined in a later paragraph, Eq. 1 will be assumed to give these elementary reactions.

Let the overall rate of each reaction in Eq. 1 be r_i . Sometimes the non-negative rates of the forward (r_{iF}) and reverse (r_{iR}) processes will also be used so that

$$r_i = r_{iF} - r_{iR} \quad (2)$$

Variables r_i , r_{iF} and r_{iR} are continuous functions of the concentrations, the dependence is given in the rate equations. It follows from these definitions that the rate of concentration change for X_j is given as:

$$\frac{d[X_j]}{dt} = \sum_{i=1}^M v_{ij} r_i \quad (j = 1, 2, \dots, N) \quad (3)$$

where $[X_j]$ represents the concentration of substance X_j .

The reaction quotient [18] of each process in Eq. 1 is defined as

$$Q_i = \prod_{j=1}^N a_j^{v_{ij}} \quad (i = 1, 2, \dots, M) \quad (4)$$

where a_j represents the activity of X_j . The activities are continuous functions of the concentrations, therefore Q_i is also a continuous function of the concentrations. The reaction quotient in the state of thermodynamic equilibrium is the equilibrium constant and will be denoted by K_i . Note that K_i does not depend on concentrations or activities.

The second law of thermodynamics states that the entropy of an isolated system cannot decrease in time. Although the law does not say anything about the magnitude of changes in time, it provides an inequality to judge whether a particular process is possible or not ('entropy as an arrow of time'). In usual closed chemical systems, constant temperature and pressure are maintained by the environment and the second law can be re-phrased by saying that the free energy (G) cannot increase in time [18]. In irreversible thermodynamics, a consequence of the second law is given by the De Donder relation [19, 20]:

$$\sum_{i=1}^M A_i r_i \geq 0 \quad (5)$$

where A_i is the chemical affinity, $(-\partial G/\partial \xi_i)_{T,p}$, for each reaction. Keeping the definition of the extent of reaction (ξ_i) in mind and using the relationship between equilibrium constants and standard free energies, Eq. 5 can be transformed to the following form (see Supporting Information):

$$\sum_{i=1}^M r_i \ln \frac{Q_i}{K_i} \leq 0 \quad (6)$$

Equation 6 can also be derived based on a more elementary line of thought in chemical thermodynamics which does not use the concept of affinities (see Supporting Information). Equation 6 is fully equivalent to the second law of thermodynamics in a closed system at constant temperature and pressure: once adherence to this equation

is demonstrated, no further investigation is necessary to show that the process does not violate the second law of thermodynamics.

There are two major reasons why Eq. 1 is assumed to be a series of elementary reactions. First, the strict definition of reaction rate ($d\xi_i/dt$) [17] only makes sense for elementary reactions because in non-elementary processes the rates of change in reactant and product concentrations are not necessarily connected through the stoichiometry of the process (see comment in Supporting Information). Second, including a non-elementary process would assume either the total absence of an intermediate or failure to account for all sources of an intermediate, both of which would render the thermodynamic analysis erroneous. Arguably, the most noted property of elementary reactions is that they adhere to the law of kinetic mass action (i.e. $r_i = \prod_{j=1}^N [X_j]^{\rho_j}$ where $\rho_j = -\nu_j$ for each $\nu_j < 0$ and $\rho_j = 0$ for all other cases). However, this property will not be important in the forthcoming analysis.

The principle of detailed equilibrium states that $r_{iR} = r_{iF}$ in equilibrium for all reactions. This is only possible if $Q_i/K_i = r_{iR}/r_{iF}$ under any conditions because the state of equilibrium can be established for every reactant composition. If $r_{iR}/r_{iF} \geq 1$, then $r_{iF} - r_{iR} \leq 0$ and vice versa, therefore

$$r_i \ln \frac{Q_i}{K_i} = (r_{iF} - r_{iR}) \ln \frac{r_{iR}}{r_{iF}} \leq 0 \quad (7)$$

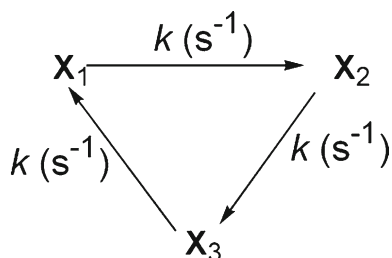
so the condition given in Eq. 6 is satisfied because all summed terms are non-positive. Therefore, adherence to the second law of thermodynamics follows from microscopic reversibility in a strictly mathematical sense.

The reverse case is more interesting. Although it is known that the principle of microscopic reversibility does not follow from the laws of thermodynamics [1], the actual connection is much more intricate. Assume that at $r_k \neq 0$ (specifically $r_k > 0$ for this line of thought) for reaction k in thermodynamic equilibrium. If reaction k is linearly independent of the other reactions, there must be an equilibrium state for the slightly different system of reactions where all the reactions and K_i values are the identical to those in Eq. 1 except the equilibrium constant of reaction k , which takes the value of $K_k^\delta = K_k + \varepsilon$. Let the rate of the reaction k be in this state r_k^δ (the rates of other reactions are not necessarily the same as r_i values, but this fact will not be important because $Q_i = K_i$ is true for all processes except reaction k). As both Q_k and r_k are continuous functions of the concentrations, a small enough ε must exist for which r_k^δ is still positive. $Q_i = K_i$, therefore $\ln(Q_i/K_i) = 0$ is true for all processes except reaction k . The thermodynamic condition required in Eq. 6 is then violated because

$$\sum_{i=1}^M r_i \ln \frac{Q_i}{K_i} = r_k^\delta \ln \frac{K_k + \varepsilon}{K_k} > 0 \quad (8)$$

A very similar line of thought can be used for the case $r_k < 0$. Therefore, if $r_k \neq 0$ for a reaction that is linearly independent of the other reactions appearing in the scheme, suitable concentrations can be found under which the reaction scheme would contra-

Scheme 1



dict the second law of thermodynamics. It follows $r_k = 0$ must hold for all reactions linearly independent of the other processes.

Finally, an example will be given where a series of linearly dependent reactions do not violate the second law of thermodynamics despite not adhering to the principle of microscopic reversibility. Consider the simple set of reactions shown in Scheme 1, which is also known as the triangle reaction. In terms of the general notations used thus far, $N = M = 3$, $\nu_{11} = \nu_{22} = \nu_{33} = -1$, $\nu_{12} = \nu_{23} = \nu_{31} = 1$, $\nu_{13} = \nu_{21} = \nu_{32} = 0$, $r_{1F} = k[X_1]$, $r_{2F} = k[X_2]$, $r_{3F} = k[X_3]$, $r_{1R} = r_{2R} = r_{3R} = 0$, and $K_1 = K_2 = K_3 = 1$. For simplicity, it is also assumed that the solution is ideal in this case and $a_1 = [X_1]/c_0$, $a_2 = [X_2]/c_0$, $a_3 = [X_3]/c_0$. The choice for the standard concentration c_0 does not influence the calculations as none of the reactions involve a change in the total amount of substance. The left side of Eq. 6 for this particular system takes the following form

$$\sum_{i=1}^3 r_i \ln \frac{Q_i}{K_i} = k[X_1] \ln \frac{[X_2]}{[X_1]} + k[X_2] \ln \frac{[X_3]}{[X_2]} + k[X_3] \ln \frac{[X_1]}{[X_3]} \quad (9)$$

Further rearrangement of Eq. 9 with the introduction of new variables $\alpha = [X_1]/[X_3]$ and $\beta = [X_2]/[X_3]$ (obviously $0 < \alpha$ and $0 < \beta$) gives:

$$\sum_{i=1}^3 r_i \ln \frac{Q_i}{K_i} = k[X_3] [(1 - \alpha) \ln \alpha + (\alpha - \beta) \ln \beta] \quad (10)$$

A simple case-by-case line of thought presented in the Supporting Information shows that

$$(1 - \alpha) \ln \alpha + (\alpha - \beta) \ln \beta \leq 0 \quad (11)$$

for any real values of α and β . Therefore, the triangle reaction shown Scheme 1 is in agreement with the second law of thermodynamics. On the other hand, a more complex network of processes containing several triangle reactions [21], which has been proposed to interpret the origin of homochirality, has been shown to violate the second law [22].

3 Conclusion

In conclusion, observing the principle of microscopic reversibility for a kinetic scheme is a satisfactory but not necessary condition to obey the laws of thermodynamics. Schemes violating microscopic reversibility may still be in agreement with the second law if they contain linearly dependent reactions. This conclusion has been reached without making assumptions about the origin of the reaction rate, therefore it is valid for every process including photochemical reactions. During considerations aimed at excluding mechanistic possibilities, it is much better to show that a scheme fails to obey the laws of thermodynamics than using the principle of microscopic reversibility.

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References

1. R.C. Tolman, Proc. Natl. Acad. Sci. USA **11**, 436 (1925)
2. R.L. Burwell Jr, R.G. Pearson, J. Phys. Chem. **70**, 300 (1966)
3. J. Chin, J. Chem. Soc. Chem. Commun. 1269 (1980)
4. W.G. Jackson, Inorg. Chem. **26**, 3004 (1987)
5. M. Tachiya, K. Seki, Chem. Phys. Lett. **243**, 330 (1995)
6. D.W. Lahti, J.H. Espenson, J. Am. Chem. Soc. **123**, 6014 (2001)
7. X. Yang, M.B. Hall, J. Am. Chem. Soc. **129**, 1560 (2007)
8. D. Colquhoun, K.A. Dowsland, M. Beato, A.J.R. Plested, Biophys. J. **86**, 3510 (2004)
9. I. Nagy, B. Kovács, J. Tóth, React. Kinet. Catal. Lett. **96**, 263 (2009)
10. D.G. Blackmond, O.K. Matar, J. Phys. Chem. B **112**, 5098 (2008)
11. D.G. Blackmond, Angew. Chem. Int. Ed. **48**, 2648 (2009)
12. D.G. Blackmond, Chirality **21**, 359 (2009)
13. I. Gutman, I. Nagypál, I. Fishtik, J. Math. Chem. **18**, 73 (1995)
14. I. Gutman, I. Nagypál, J. Math. Chem. **19**, 193 (1996)
15. I. Nagypál, E. Hoffmann, I. Gutman, I. Fishtik, Pure Appl. Chem. **70**, 583 (1998)
16. E.A. Hoffmann, I. Nagypál, Phys. Chem. Chem. Phys. **3**, 3107 (2001)
17. K.J. Laidler, Pure Appl. Chem. **68**, 149 (1996)
18. P.W. Atkins, *Physical Chemistry, 6th ed* (Oxford University Press, Oxford, 1998)
19. Th. De Donder, *L’Affinite* (Gauthier-Villars, Paris, 1927)
20. W.L. Holstein, M. Boudart, J. Phys. Chem. B **101**, 9991 (1997)
21. R. Plasson, H. Bersini, A. Commeyras, Proc. Natl. Acad. Sci. USA **101**, 16733 (2004)
22. G. Lente, React. Kinet. Catal. Lett. **95**, 13 (2008)