Thermodynamic insights into chemical energy conversion

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Abstract

Non-equilibrium thermodynamics has a unique role to play in the development of sustainable technology, for it can effectively reveal and deal with the fundamental limitations of specific energy- and material conversions. One major aspect of sustainable technology is unmistakably efficiency, and hence a good insight into the behavior and performance of energy-conversion systems is essential. One area that has our particular interest is energy transfer by the direct coupling of chemical reactions. This mechanism is prominent in the metabolism of living systems, for which we have identified exceptional thermodynamic performances. With a simple, but useful, model of the irreversible thermodynamics of the coupled-reaction system, we can reveal much of the essential behavior and obtain some meaningful insights into high-performance energy conversion. Focus will be on the rate of energy conversion, entropy generation, and thermodynamic efficiency. We relate our findings to some well-known optimization strategies in engineering, such as the equipartitioning of driving forces and entropy generation minimization.

Introduction

All processes are subject to the constraints of the laws of thermodynamics, and particularly the second law of thermodynamics can impose limitations to energy- and material conversions that are not immediately evident. Equilibrium and non-equilibrium thermodynamics can reveal and quantify these limitations, and thus we can obtain meaningful insights into the thermodynamic performance of technological processes. When including second-law limitations, technological processes typically prove to be quite inefficient, suggesting that there is huge theoretical potential for improvement.

In contrast, our thermodynamic analyses of several intracellular processes have shown that thermodynamic efficiency of biochemical energy conversion is exceptionally high. The high performance seems to be related to the direct stoichiometric coupling between thermodynamically favorable and unfavorable chemical reactions, and to the relatively low spontaneity of the coupled reaction. Since biochemical energy transfer may stand as example for future technological energy transfer, aspects of its thermodynamic optimization could be of relevance to the field of sustainable engineering.

Several methods have been suggested for optimizing conventional energy-transfer processes such as heat engines, heat pumps, and certain energy-storage systems. These strategies include reducing and equipartitioning driving forces, and minimizing the rate of entropy generation (Bejan, 1996). We have wondered to what extent these methods can also be used to optimize energy conversion in coupled (bio)chemical reactions. To explore this, we consider a basic model of the coupled reaction and analyze its performance under varying conditions. For the complete description of this work and all the graphical representations of the results of the model, we refer to the original paper (Lems, Van der Kooi, and de Swaan Arons, 2003).

Model for chemical energy transfer

A system of chemical reactions is considered as given in figure 1. Chemical energy is transferred in the coupled chemical reaction (C+X$\rightarrow$D+Y) in which the thermodynamically favorable (downhill) reaction of compound C to D drives the thermo-dynamically unfavorable (uphill) reaction of compound X to Y. Westerhof (1987) also describes energy

transfer in coupled chemical reactions, but the model presented here is essentially different in two ways.

First, the model uses a *nonlinear* relation to describe the dependence of the reaction rate on the driving force of the reaction. At the constant temperature, the driving force is determined by the negative Gibbs energy change of the reaction, which is indicated as the reaction affinity A (i.e. $A=-\Delta G_{reaction}$). The nonlinear relation follows from the work of Eyring (1935, 1963) and De Donder (1927). A linear relation is often used, but this approximation only applies at very small driving forces, i.e. close to equilibrium conditions (see for example Førland, Førland, and Kjelstrup, 2001). Hence, the nonlinear relation describes the thermodynamic behavior of a chemical reaction more realistically at non-equilibrium conditions.

Secondly, the model includes two leak reactions (C→D and Y→X) which are independent from the coupled reaction: instead of including leakage via a constant coupling factor (see Westerhof, 1987), the leak reactions are determined by their own nonlinear force-flow relation. The rates of the leak reactions relative to the rate of the coupled reaction are determined by the difference in the activation Gibbs energies (ΔG^{*}), which is expressed by the kinetic parameter $\lambda=[\Delta G^{*}_{leak}-\Delta G^{*}_{coupled}]/RT$. For simplicity, both leak reactions are considered to have the same activation Gibbs energies. When assuming the difference in activation energies to be mainly the result of catalysis of the coupled reaction, λ expresses the extent to which the coupled reaction is catalytically favored over the leak reactions.
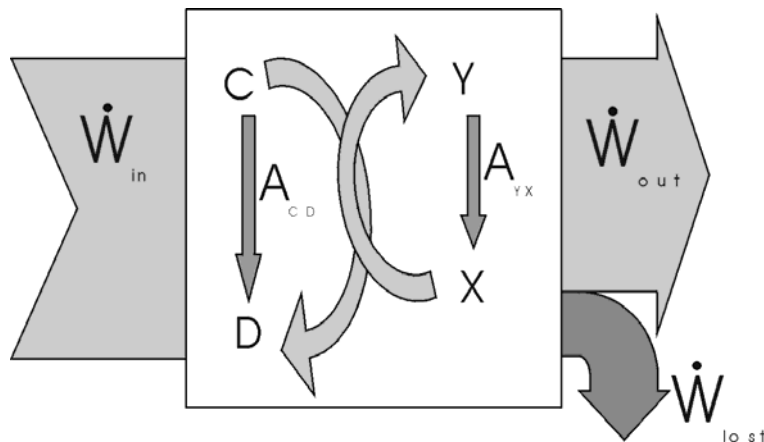

Figure 1: system of reactions and the input, output, and loss of chemical work potential.

The performance of the model is analyzed at different values of λ by varying the affinity of the coupled reaction, $A_{coupled}$, which is the driving force for the chemical energy transfer. The affinity A_{CD} of the work-supplying reaction C→D is fixed at 50 kJ/mol, resembling the situation in actual biochemical energy-transfer reactions involving ATP at intracellular conditions. Below, we discuss the results obtained on output of chemical work potential, thermodynamic efficiency, and entropy generation.

Work output

The work-output rate is the amount of chemical work potential exiting the reaction system per unit of time (in the form of compound Y). At a given value λ, the maximum work-output rate is achieved when there is a balance between dissipation and transfer of chemical energy (i.e. at intermediate values of $A_{coupled}$), but the position of the maximum does not follow from an equipartitioning rule, which requires that half the available driving force (in

this case A_{CD}) must be dissipated. Indeed, maxima are not found anywhere near the equipartitioning point where $A_{coupled}$=25 kJ/mol. The reason for the failure of the equipartitioning rule is the effect of the leak reactions and the nonlinear behavior of the coupled reaction. Without the leakage and the nonlinearity, the complex requirement for maximum work-output rate can be shown to reduce to the simple equipartitioning rule of $A_{coupled}$=½·A_{CD}. Hence, the equipartitioning of driving forces can only really lead to the maximum performance at these special conditions.

At a critical value of λ, we observe a jump from one class of optima to another. This remarkable result of nonlinear behavior reflects the existence of two opposing optimization strategies in the energy conversion. At high values of λ, the superior strategy is to transfer energy efficiently at low driving force $A_{coupled}$ and avoid energy dissipation in the coupled reaction. At very low values of λ however, the best strategy is to transfer energy fast at high driving force $A_{coupled}$ to keep up with the high rates of energy dissipation in the leak reactions. By far the best performances are obtained with efficient transfer of energy at high values of λ, where the maximum work outputs are obtained at modest driving forces.

Thermodynamic efficiency

The thermodynamic efficiency is the work-output rate as a fraction of the work-input rate. In the absence of leak reactions (i.e. when λ=∞), the efficiency increases continually with decreasing values of $A_{coupled}$. Although in practice some energy dissipation in the coupled reaction is always required to transfer energy at a non-zero rate, the thermodynamic efficiency can theoretically reach unity when $A_{coupled}$ is reduced to zero. Hence, under these 'ideal' circumstances, a strategy of reducing the driving forces of the energy-conversion process *always* improves the efficiency (although of course the conversion rate decreases).

Real energy-conversion systems however inevitably include leak processes, and reducing the driving forces of the energy-conversion process will then at some point lead to a drop in the efficiency: as the driving force, $A_{coupled}$, decreases, energy conversion becomes slower and the relative influence of the leak reactions increases. In the end, this increasing effect of the leak reactions always outweighs the efficiency benefits of operating the coupled reaction at a smaller driving force. Hence, a strategy of reducing driving forces to improve the efficiency will not always work, and will in fact eventually fail.

Entropy generation

The entropy generation related to the operation of the chemical reaction system equals the entropy generation in the coupled reaction plus that in the two leak reactions. Although there are faint minima in the entropy-generation rate, the driving force, $A_{coupled}$, at which these minima are obtained do not coincide with the driving force(s) at which the work-output rate and the thermodynamic efficiency are optimal, as was observed by Bejan (1996) for some models of heat-driven processes. In fact, at most values of λ, minimization of the entropy-generation rate leads to a particularly poor performance. Clearly, a strategy of entropy generation minimization fails to optimize the performance of the chemical reaction system considered.

It is true that the total rate of entropy generation is directly related to the rate at which chemical energy is dissipated, and therefore it must have a direct relation to the work-output rate and the thermodynamic efficiency. However, the fundamental equations show that entropy generation is not the only factor determining the performance of an energy-conversion system: the work-input rate is the other main factor, which can also vary with how the energy-conversion process is operated. We find that minimizing the total rate of entropy generation *only* leads to maximum work-output rate, and in fact simultaneously to maximum thermodynamic efficiency, in cases where the work-input rate is fixed and hence

independent of the operation of the energy-conversion system (e.g. solar power plant). When the work-input rate is not fixed, as in the chemical reaction system, minimum entropy generation, maximum power output, and maximum thermodynamic efficiency are three distinct points in the operation of the energy-conversion process.

High-performance energy conversion

It follows from the considered reaction model that higher values of the kinetic parameter λ lead to higher efficiencies and work-output rates over the entire interval of the driving force $A_{coupled}$. This shows that, although much attention is on finding the optimum driving force of the conversion process (and leak processes are often ignored), λ is the primary determinant of a good performance of the chemical system.

In biochemical processes, the activation barriers of specific reactions can be lowered by enzymes to an amount ranging roughly from 30 to 100 kJ/mol (Nelson & Cox, 2000), corresponding to an increase in reaction rate by a factor of 10^5 to 10^{17}. Although we must be careful to directly apply these values into the reaction model, such catalytic effects should allow for exceptional performances. Yet, there is no single driving force where the performance is optimal. Rather, the model suggests an optimal region where there is a trade-off between efficiency and work-output rate. Within this region, the energy conversion can be performed at smaller driving forces, where the system is more efficient, or at higher driving forces, where the system delivers more output per unit of time. Moving outside the region is always suboptimal, since a decrease in efficiency is accompanied by a decrease in work-output rate.

Conclusions

By including nonlinear force-flow relations and independent leak reactions into a basic model of a coupled chemical reaction, some insights were obtained on the optimization of (bio)chemical energy conversion. First, the work-output rate of the chemical reaction system is highest when there is a balance between transfer and dissipation of energy, but the optimum does not follow from the equipartitioning of driving forces. It is found that such a principle, as observed in models of heat-driven systems, only works when parallel leak processes are absent and the force-flow behavior of the conversion process is linear. Second, it is found that a strategy of reducing the driving force of the coupled reaction to increase the efficiency of energy conversion will eventually fail, because of the increasing relative effect of the leak reactions. Third, minimizing the rate of entropy generation of the system does not optimize the performance of the chemical reaction system. It is found that this only leads to maximum efficiency and work-output rate when the work-input rate is fixed, i.e. independent of how the system is operated.

The kinetic factor λ sets the limits for, and is thereby the primary determinant of, the performance of the chemical system. Higher values of λ yield higher efficiencies and work-output rates at every applied driving force, and, depending on the value of λ, one of two main energy-conversion strategies (i.e. fast or efficient conversion) leads to the optimal performance of the system. By far the best performances are reached with efficient conversion, although no single point of operation can be considered optimal. Rather, there is an optimal window of driving forces where efficiency can be sacrificed for higher work-output rates, and vica versa.

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