Equilibrium Chemical Engines

Tatsuo SHIBATA and Shin-ichi SASA

Department of Pure and Applied Sciences, University of Tokyo.
Komaba, Meguro-ku, Tokyo 153, Japan

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An equilibrium reversible cycle with a certain engine to transduce the energy of any chemical reaction into mechanical energy is proposed. The efficiency for chemical energy transduction is also defined so as to be compared with Carnot efficiency. Relevance to the study of protein motors is discussed.

KEYWORDS: Chemical thermodynamics, Engine, Efficiency, Molecular machine.

§1. Introduction

The molecular machine in biological systems works as a chemical energy transducer. For instance, the protein motors such as myosin and kinesins, or flagellar motor produce mechanical energy as they consume the chemical energy provided by hydrolysis of ATP or proton density gradient. Some other proteins, such as enzymes or pump proteins of membrane transportation, can be also thought as chemical energy transducer in which energy input and output are both chemical. Recently various phenomenological models for protein motors have been studied and the thermodynamic interpretation for these models have been presented. However, the models, in which chemical reaction is taken into account, are scarcely proposed. While the energetics of models, in which chemical reaction is explicitly supposed, may be future task, none have discussed an equilibrium cycle associated with any chemical reaction, as Carnot considered Carnot cycle for thermal energy transduction. Also the notion of energy transduction efficiency from chemical to mechanical has never been stated explicitly. These will be important when we compare the energy transduction in molecular machines with macroscopic thermodynamics.

In this Paper, we discuss how we should define a proper chemical energy transduction efficiency and how we construct an engine which gives its maximal value. In §2, a chemical engine to transduce energy of arbitrary chemical reaction into mechanical energy is proposed. In §3, we review the chemical thermodynamics of the processes involving the chemical reaction. Equilibrium chemical reaction is also presented. In §4 and §5, we show an equilibrium reversible cycle using the chemical engine as to correspond to the idealized cycle for heat engines which Carnot considered. Further we propose efficiency for chemical energy transduction, and show its maximum value. In §6, the heat flow associating with particle flow is studied. In §7, we study some applications to compare energetic behavior of molecular engines with macroscopic engines. The paper concludes in §8 with a discussion about efficiency.

§2. Chemical Engine

Consider $n$ chemical components among which chemical reaction

$$\sum_{i=1}^{n} \nu_i M_i = 0 \quad (2.1)$$

takes place, where $M_i$ is the symbol for the $i$’th chemical component, and $\nu_i$ is stoichiometric coefficient which is positive when the component is a product in the chemical reaction, while negative when the component is a reactant. For convenience, let the chemical formula be written as the spontaneous reaction takes place in the direction that the products increase when the chemical affinity

$$A = -\sum_{i} \nu_i \mu_i \quad (2.2)$$

is positive, where $\mu_i$ is the chemical potential of the $i$’th component.

We enclose the components in a container (reaction box), which has a piston to change the volume $V$ and the pressure $p$ in touch with a heat bath, so that the chemical reaction takes place and the energy of chemical reaction is transduced into mechanical energy (see Fig.1).

The container can also take any $i$’th component in and out from source which contains only the $i$’th component at the chemical potential $\mu_{0,i}$. We assume that an ideal semi permeable membrane to the $i$’th component which separate the container and the source is completely impermeable to all other components. This configuration is similar to Van’t Hoff reaction box.

§3. Equilibrium Chemical Reaction

We review the chemical thermodynamics of processes involving chemical reaction eq. (2.1).

The change of Gibss’s free energy $G = G(T, p, \{N_i\})$
we can extend eq. \((3.2)\) to the form
\[
dN_j = \nu_j d\xi + dN_j^{\text{ext}}.
\] (3.7)

Therefore from eqs. \((3.1)\) and \((3.4)\) we obtain
\[
dG = -SdT + Vdp + \mu_{0,j}dN_j^{\text{ext}}.
\] (3.8)

By the two equilibrium conditions \(\mu_j = \mu_{0,j}\) and eq. \((3.4)\), the number of independent variables in equation \(\mu_i = \mu_i(T, p, \xi, N_j^{\text{ext}})\) is reduced to two. In this way, we can regard \(\xi\) and \(N_j^{\text{ext}}\) as dependent variables of \(T\) and \(p\). We thus obtain
\[
dG = \left(-S + \mu_{0,j} \frac{\partial N_j^{\text{ext}}}{\partial T}\right) dT + \left(V + \mu_{0,j} \frac{\partial N_j^{\text{ext}}}{\partial p}\right) dp.
\] (3.9)

### §4. Equilibrium Reversible Cycle

We show how an equilibrium reversible cycle \(C\) is realized by employing the chemical engine presented in §2.

In the argument below, we suppose that the container is always kept in touch with a heat bath and that all processes are quasi-static.

At the initial state \(\mu_1\) is assumed to equal to \(\mu_{0,1}\). While the equilibrium conditions is kept, the volume \(V\) is shifted so that the container can absorb the first component from the source. Next the source of the \(i\)th component is separated from the container and the volume \(V\) is changed until \(\mu_2\) equals to \(\mu_{0,2}\). After that, let the container touch with the source for the second component, and the volume \(V\) is shifted so that the container can absorb the second component, as in the case of first component, and so forth.

Repeating the similar procedure, we have the following cycle \(C\), which consists of \(2n\) steps, let \(i\) be 1, 2, \(
\vdots\), \(n\).

- \(2i-1\)th step: Let the container be kept in touch with the source of the \(i\)th component. While the equilibrium conditions is kept, the volume \(V\) is changed so that the container can absorb the component. Note that an amount of the component absorbed into the container is positive when the component is reactant while negative when product.

- \(2i\)th step: Separating the source from the container, the volume \(V\) is changed until \(\mu_{i+1}\) comes to be \(\mu_{0,i+1}\).

The \(i\) is assumed to set in order, but the order is allowed to set arbitrary. After \(2n\)th step, one cycle will be completed by changing \(\mu_1\) until \(\mu_1\) equals \(\mu_{0,1}\), so as to bring the system back to its initial state.

### §5. Efficiency

We discuss energy transduction efficiency for chemical engines. First we notice that we should define the efficiency so as to compare chemical engines with heat engines. In the case of heat engines with two heat baths of different temperature \((T_+ > T_-)\), the efficiency for heat engines was defined as
\[
\eta_{\text{heat}} = \frac{W}{Q_+},
\] (5.1)

where the system absorbs the heat \(Q_+\) from the heat bath and transduces into the mechanical energy \(W\).
we obtain
\[ W = \int \sum_{\nu_i < 0} \nu_i \mu_{0,i} \, d\xi = A_0 \int d\xi, \quad (5.9) \]
where \( A_0 \) is chemical affinity of sources
\[ A_0 = -\sum_i \nu_i \mu_{0,i}. \quad (5.10) \]

Equation (5.9) is the work within one cycle transformed from the energy of chemical reaction. Note that the result is independent of ratio of components in the container, or nature of working substance, e.g. it does not depend on it whether or not the substance is ideal.

From eqs.(5.8) and (5.9), the efficiency of the cycle \( C \) is given by
\[ \eta = \frac{-\sum_i \nu_i \mu_{0,i} \int d\xi}{\sum_{\nu_i > 0} \nu_i \mu_{0,i} \int d\xi} = \frac{A_{0+} - A_{0-}}{A_{0+} - A_{0-}}. \quad (5.11) \]

Carnot cycle gives the maximum efficiency
\[ \eta_{heat} = \frac{T_+ - T_-}{T_+}. \quad (5.2) \]

In the case of chemical engines, the efficiency should be defined as
\[ \eta = \frac{W}{G_+} \quad (5.3) \]
with the free energy \( G_+ = \sum_{\nu_i > 0} \mu_{0,i} N_i^{ext} > 0 \) absorbed by the container from the sources of the products(\( \nu_i > 0 \)), where the container absorbs an amount \( N_i^{ext} \) of the \( i \)th source (see Fig.2).

We now calculate the work \( W \) and \( G_+ \) for the cycle \( C \). Since the cycle \( C \) works isothermally, thermodynamic relation for each steps is written as
- \( 2i-1 \)th step:
  \[ dG = V dp + \mu_{0,i} dN_i^{ext}, \quad (5.4) \]
- \( 2i \)th step:
  \[ dG = V dp. \quad (5.5) \]

where we have used eqs.(5.5) and (5.8).

From eqs.(5.4) and (5.5) we get
\[ \int dG = \int V dp + \sum_i \int_{2i-1}^{2i} \mu_{0,i} dN_i^{ext} = 0, \quad (5.6) \]
where the integral is taken over one cycle. Thus the work \( W \) in the cycle \( C \) is given by
\[ W = -\int V dp = \sum_i \mu_{0,i} \int_{2i-1}^{2i} dN_i^{ext}. \quad (5.7) \]

Since \( N_i \) brings back to its initial value after one cycle, we obtain
\[ \int dN_i = \nu_i \int d\xi + \int_{2i-1}^{2i} dN_i^{ext} = 0, \quad (5.8) \]
where we have used eq.(3.7).

Substituting eq.(5.8) into eq.(5.7) yields
\[ W = -\sum_i \nu_i \mu_{0,i} \int d\xi = A_0 \int d\xi, \quad (5.9) \]
where \( A_0 \) is chemical affinity of sources
\[ A_0 = -\sum_i \nu_i \mu_{0,i}. \quad (5.10) \]

Equation (5.9) is the work within one cycle transformed from the energy of chemical reaction. Note that the result is independent of ratio of components in the container, or nature of working substance, e.g. it does not depend on it whether or not the substance is ideal.

From eqs.(5.8) and (5.9), the efficiency of the cycle \( C \) is given by
\[ \eta = \frac{-\sum_i \nu_i \mu_{0,i} \int d\xi}{\sum_{\nu_i > 0} \nu_i \mu_{0,i} \int d\xi} = \frac{A_{0+} - A_{0-}}{A_{0+} - A_{0-}}. \quad (5.11) \]

where \( A_{0-} = \sum_{\nu_i < 0} \nu_i \mu_{0,i} \) and \( A_{0+} = -\sum_{\nu_i > 0} \nu_i \mu_{0,i} \).

Note that the chemical affinity is decomposed as \( A_0 = A_{0+} - A_{0-} \).

If there were the cycle \( C' \) whose efficiency is higher than eq.(5.11), by coupling this cycle \( C' \) with the above cycle \( C \), the chemical reaction could take place in a direction opposite to that predicted by its own affinity, and as a result, the total free energy in the sources increased spontaneously. Since this violates the 2nd thermodynamic law, the cycle \( C \) gives the maximum efficiency.

§6. Heat Flow

So far, we have been attention to the free energy flow between the container and the sources in the cycle \( C \). We next consider the heat flow among the container, the sources, and the heat bath.

Processes in the sources and the heat bath are assumed to be quasi-static. When the entropy per one molecule of the \( i \)th component in the source is denoted by \( s_i \), the thermodynamic relation for the \( i \)th source is given by
\[ dU_i = -(T s_i + \mu_i) dN_i^{ext}, \quad (6.1) \]
in which we suppose that changes of volume in the sources is so small that these are negligible. We can include the effect of volume change if necessary. In this formula, \( (T s_i + \mu_i) \) can be interpreted as the enthalpy per one molecule of the \( i \)th sources \( s_i \). The thermodynamic relation for the heat bath is given by
\[ dU_H = T dS_H. \quad (6.2) \]

Since the energy conservation law gives \( \Delta U + dU_i + dU_H = W \) where \( \Delta U \) denotes the energy change in the container, we obtain
\[ \Delta U = -T dS_H + h_i dN_i^{ext} - W. \quad (6.3) \]

Thus, in one cycle,
\[ W = Q + \sum_i h_i N_i^{ext}, \quad (6.4) \]
where \( Q = -T dS_H \) is heat flow from the heat bath. We should note that particle transportation is inevitably accompanied by heat flow from the source (see Fig.3).
Fig. 3. schematic figure of the heat flow. Particle transportation \( h_iN_+ \) is inevitably accompanied by heat flow \( TsN \). The total energy absorbed by the container from the source equals to enthalpy \( hN \). With the heat \( TsN \) from the source, heat \( Q \) is transported from the heat bath into the container.

Under the equilibrium condition of the container, when the container touches with the \( i \)’th source and the heat bath, the entropy change in the heat bath is given by

$$dS_H = -dS + s_i dN_{ext}^i. \quad (6.5)$$

Note that the heat flow from the heat bath into the container is not \( TdS \). Kitahara has developed similar argument in the context of heat engine with particle flow.

By integrating eq. (6.5), the heat absorbed by the container from the heat bath in one cycle \( Q \) is written as

$$Q = -T \sum_i s_i N_{ext}^i, \quad (6.6)$$

which can be positive or negative depending on the detail of the chemical reaction. Note that because of the isothermal condition and \( \oint dS = 0 \), the total heat absorbed by the container is equal to zero, whether the chemical reaction eq. (6.5) is endothermic or exothermic. Therefore, the sources absorb the heat \( Q \) from the container as expressed in the form of the right handed side of eq. (6.6).

§7. Application

To analyze the difference between molecular motors and macroscopic engines, molecular motors should be compared with this idealized cycle, just as Feynmann’s ratchet is compared with Carnot cycle. The cycle as we have discussed above is the most ideal than any other engines with chemical reaction including molecular motors such as myosin or kinesins. For molecular motors with the hydrolysis reaction of ATP\( \rightarrow \)ADP+P, the maximum efficiency becomes

$$\eta = \frac{\mu_{ATP} - \mu_{ADP} - \mu_P}{-\mu_{ADP} - \mu_P}. \quad (7.1)$$

Because chemical potential is negative and is increased with concentration, high concentration of ATP in the living systems makes this efficiency higher.

On the other hand, flagellar motors seems to consume the potential energy in the proton density gradient without chemical reaction. The above result can be applicable to this case. Suppose that the working substance consists of a simple chemical component \( M \) and there are two sources whose chemical potentials are \( \mu_- \) and \( \mu_+ \). Even in such a case, we can regard particle transportation between two sources as a sort of chemical reaction in the following way. When a molecule in each source (with the values of \( \mu_- \) and \( \mu_+ \)) is denoted by \( M_- \) and \( M_+ \) respectively, transportation between two sources can be expressed by

$$M_- \rightarrow M_+ \quad (7.2)$$

in cycle, the maximum efficiency \( \eta \) is

$$\eta = \frac{\mu_+ - \mu_-}{\mu_+}. \quad (7.3)$$

For molecular engines such as enzymes, pump proteins of membrane transport, and mitochondrial electron transport chain, several chemical reactions take place simultaneously. We then consider a cycle in which several chemical reaction take place simultaneously in the container. Consider the \( j \)’th chemical reaction

$$\sum_{i=1}^{n_j} \nu_{ji} M_{ji} \rightleftharpoons 0, \quad (j = 1, 2, 3, \cdots m), \quad (7.4)$$

where \( M_{ji} \) is the \( i \)’th component of the \( j \)’th reaction, \( \nu_{ji} \) is stoichiometric coefficient, and \( m \) is the total number of reactions. Then the work in one cycle is given by

$$W = \sum_{j=1}^{m} A_{0j} \oint d\xi_j, \quad (7.5)$$

with the chemical affinity of the \( j \)’th reaction \( A_{0j} = -\sum_{i=1}^{n_j} \nu_{ji} \mu_{0ji} > 0 \), where \( \mu_{0ji} \) is chemical potential of the source of \( M_{ji} \), and \( \oint d\xi_j \) is extent of the reaction. The maximum efficiency \( \eta \) is given by

$$\eta = \frac{\sum_{j=1}^{m} (A_{0j+} - A_{0j-}) \oint d\xi_j}{\sum_{j=1}^{m} A_{0j+} \oint d\xi_j}, \quad (7.6)$$

where \( A_{0j-} = \sum_{\nu_{ji} < 0} \nu_{ji} \mu_{0ji} \), and \( A_{0j+} = -\sum_{\nu_{ji} > 0} \nu_{ji} \mu_{0ji} \). Note that in this case the maximum efficiency depends on how to operate the cycle.

With regards to the molecular engines with more than one chemical reaction such as enzyme, pump proteins of membrane transport, and mitochondrial electron transport chain, these might be thought as chemical energy transducers which produce chemical energy rather than mechanical energy. When the container absorbs free energy \( G_j \) from the sources for the components in the \( j \)’th chemical reaction, \( G_j \) is expressed by

$$G_j = \sum_i \nu_{ji} N_{ext}^{ji}, \quad (7.7)$$

where the container absorbs an amount \( N_{ext}^{ji} \) of \( M_{ji} \).
Therefore the inequality
\[
\sum_{j=1}^{m} G_j \geq 0
\]
(7.8)
should be satisfied, when the process is spontaneous. Under this condition, \( G_j \) can be negative, and as a result the total free energy in the sources associated with this \( j \)'th reaction increases in one cycle. Let us call the chemical reaction which satisfies \( G_j > 0 \) “input chemical reaction”, while “output chemical reaction” for \( G_j < 0 \). In this cycle, the energy of input chemical reaction is transformed into the energy of output chemical reaction. In other words, the container catalyzes the output chemical reaction which can not take place spontaneously, utilizing the energy of input chemical reaction. The catalytic energy efficiency \( \zeta \) may be defined by
\[
\zeta = \frac{-\sum_{j=0}^{m} G_j}{\sum_{j=0}^{m} G_j}.
\]
(7.9)
In quasi-static process, all the chemical energy of input chemical reaction can be transformed into the energy of output chemical reaction. Thus the maximum catalytic efficiency is 1. Note that the stoichiometric relation between the components associated with the different chemical reactions in general depends on the process. For instance, in the case of \( m = 2 \), the ratio of the extent in the two reaction \( \frac{\int d\xi_1}{\int d\xi_2} \) depends on process.

§8 Discussion

Before concluding this Paper, we discuss the definition of efficiency. The efficiency
\[
\eta' = \frac{W}{G_+ + G_-}
\]
(8.1)
has been used in some bibliography. The maximum value of this quantity turns to be 1 from the discussion in §5. We should consider that this efficiency eq. 8.1 can be used to compare the energy loss by dissipation accompanied with irreversible heat generation in different cycles under the same condition. On the other hand, we consider that the efficiency eq. 5.3 presented in this Paper can be applicable to compare different cycles under different conditions, while the efficiency eq. 5.3 can be also used for cycles under the same condition. Therefore, we believe the latter definition eq. 5.3 is preferable than former eq. 8.1 to compare the efficiency of cycles.

Thermal ratchet engines such as Feynmann’s ratchet are microscopic heat engines, which rectify thermal fluctuation to generate mechanical energy. Thermal fluctuation is believed to play an important part in function of proteins. Thus the thermal ratchet engines might bring some notions of energy transduction in proteins. However, while high efficiency in molecular motors pointed out, it has been shown that the efficiency of the thermal ratchet engines is much less than Carnot efficiency. While thermal energy transduction has not been understood well, energy transduction with chemical reaction and heat might be far beyond our comprehension. In order to develop notion of chemical energy transduction in molecular systems, it is a future problem to construct the comprehensive model for motor proteins in which chemical reaction should be explicitly supposed. The efficiency we have proposed in this paper may be one of the useful property to compare models with actual motor proteins. We believe that our study here may provide systematic tool for discussing the efficiency in these systems.

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