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Endoreversible four-mass-reservoir chemical pump with diffusive mass transfer law

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Abstract
The performance of an isothermal endoreversible four-mass-reservoir chemical pump, in which the mass transfer obeys diffusive law, is analyzed and optimized in this paper. The relation between the rate of energy pumping and the coefficient of performance of the isothermal chemical pump is derived by using finite-time thermodynamics. Moreover, the optimal operating regions and the influences of some parameters on the performance of the cycle are studied. The results obtained herein can provide some new theoretical guidelines for the optimal design of a class of apparatus such as mass exchangers, and electrochemical, photochemical, and solid-state devices, as well as fuel pumps for solar-energy conversion systems.

Keywords: Finite time thermodynamics; Four-mass-reservoir chemical pump; Finite-rate mass transfer; Diffusive mass transfer law; Coefficient of performance; Rate of energy pumping.

1. Introduction
In the recent years, finite-time thermodynamics [1-16] was applied to the performance study of various thermodynamic cycles and devices. It has also been extended to the cyclic devices driven by mass flow, such as chemical reactions and chemical engines, by many researchers [17-28]. Heat engines generate work from differences in temperature. Similarly, chemical engines generate work from differences in chemical potentials. Chemical potential and mass transfer in chemical engines play the analogous roles of temperature and heat current in heat engines. de Vos [4, 17-19] investigated the performance of solar cells, chemical reactions and solar energy conversion processes and devices. Tsirlin et al. [20] analyzed the performance of chemical reactors. Gordon [21] and Gordon and Orlov [22] obtained the maximum work output [21] and the maximum power output of a class of isothermal endoreversible chemical engines with the sole irreversibility of mass transfer. Chen et al. [23, 24] derived the optimal relation between the power output and the second law efficiency of the isothermal endoreversible chemical engines with the sole irreversibility of mass transfer [23] and analyzed the effect of mass leakage on the performance of isothermal chemical engines [24]. Chen et al. [25, 26] established a new model of a class of combined-cycle isothermal endoreversible chemical engines, derived the optimal relation between the power output and the second law efficiency of the combined-cycle isothermal endoreversible chemical engines with the sole irreversibility of mass transfer [25], and analyzed the effect of mass leakage on the performance of combined-cycle isothermal chemical engines [26]. Lin et al. [27] established a model of a generalized irreversible isothermal chemical engine with irreversibility of mass transfer, mass leakage

and internal loss, and derived the optimal relation between the power output and the first law efficiency of the irreversible isothermal chemical engine. Tsirlin et al. [28] also derived the minimum entropy generation rate and the maximum power output of a class of isothermal endoreversible chemical engines. The inverse cycle of a heat engine is a heat pump cycle or a refrigerator cycle. Similarly, the inverse cycle of a chemical engine is a chemical pump cycle or a chemical potential transformer cycle. Lin and Chen. [29] studied the performance of the endoreversible and irreversible two-mass-reservoir chemical pump with the irreversibility of mass transfer and the mass leak. Lin et al. [30] studied the performance of the irreversible two-mass-reservoir chemical pump with the irreversibility of mass transfer, mass leakage and internal irreversibility. Lin et al. [31] established an endoreversible three-mass-reservoir chemical pump model considering the effects of mass transfer irreversibility, and studied its performance with linear mass transfer law. Wu et al. [32] studied the performance of a three-mass-reservoir chemical pump with the irreversibility of mass transfer and mass leak. Xia et al. [33] established an endoreversible four-mass-reservoir chemical pump model considering the effects of mass transfer irreversibility, and studied its performance with linear mass transfer law. Chen et al. [34] established a generalized irreversible four-mass-reservoir chemical pump model considering the effects of mass transfer, mass leakage and internal irreversibility, and studied its performance with linear mass transfer law.

In the modelling and optimization mentioned above [21-34], the mass transfer between the mass reservoirs and the chemical engine or chemical pump is always assumed to be obey linear mass exchange law, i. e $\Delta N \propto \Delta\mu$, where ΔN is the exchanged mass and $\Delta\mu$ is the chemical potential difference. However, chemical converters that are governed by diffusive mass transfer are inherently more efficient than those governed by linear mass transfer [22]. So it is necessary to investigate the performance of chemical converters which obey the more general and practical mass transfer law: the diffusive mass transfer law. Recently, Chen et al. [35] and Xia et al. [36, 37] modeled and optimized the performance of endoreversible chemical engines [35], endoreversible two-mass-reservoir chemical pumps and endoreversible three-mass-reservoir chemical potential transformer with the diffusive mass transfer law.

The purpose of this paper is to model and optimize the performance of an endoreversible four-mass-reservoir chemical pump by assuming that the mass transfer between the cyclic working medium and the mass reservoirs obeys nonlinear law which is more general and practical, i. e. the diffusive mass transfer law $\Delta N \propto \Delta(\mu / kT)$, where k is Boltzmann's constant and T is temperature. The rate of energy pumping versus the coefficient of performance (COP) characteristic is obtained by numerical calculations.

2. Chemical pump model

The schematic diagram of an endoreversible chemical pump operated among four mass-reservoirs is shown in Figure 1. In the figure, parameters μ_H, μ_L, μ_O, and μ_M are, respectively, the chemical potentials of the four mass-reservoirs and they supposed to be constant and obey the relation: $\mu_H > \mu_O > \mu_M > \mu_L$. The parameters μ_1, μ_2, μ_3 and μ_4 are, respectively, the chemical potentials of the chemicals involved in the four processes in the cycle's working- medium. Because of the existence of finite-rate mass transfer, μ_1, μ_2, μ_3 and μ_4 are, respectively, different from those of the four mass-reservoirs. The parameters ΔN_1, ΔN_2, ΔN_3 and ΔN_4 are, respectively, the amounts of mass exchange between the cyclic working medium and the four mass-reservoirs at chemical potentials μ_H, μ_L, μ_O, and μ_M per cycle. The parameters h_1, h_2, h_3 and h_4 are, respectively, the mass-transfer coefficients between the cycle's working medium and the mass reservoirs at chemical potentials μ_H, μ_L, μ_O, and μ_M. The parameters t_1, t_2, t_3 and t_4 are the corresponding times spent undergoing the four mass transfer processes. The cycle period is:

$$\tau = t_1 + t_2 + t_3 + t_4 \tag{1}$$

It is assumed that the mass exchange obeys the diffusive mass transfer law of nonlinear irreversible thermodynamics, i.e.

$$\Delta N_1 = h_1(\exp\tfrac{\mu_H}{kT} - \exp\tfrac{\mu_1}{kT})t_1,\ \Delta N_2 = h_2(\exp\tfrac{\mu_L}{kT} - \exp\tfrac{\mu_2}{kT})t_2$$

$$\Delta N_3 = h_3(\exp\tfrac{\mu_3}{kT} - \exp\tfrac{\mu_O}{kT})t_3,\ \Delta N_4 = h_4(\exp\tfrac{\mu_4}{kT} - \exp\tfrac{\mu_M}{kT})t_4 \tag{2}$$

where k is Boltzmann's constant and T is temperature.

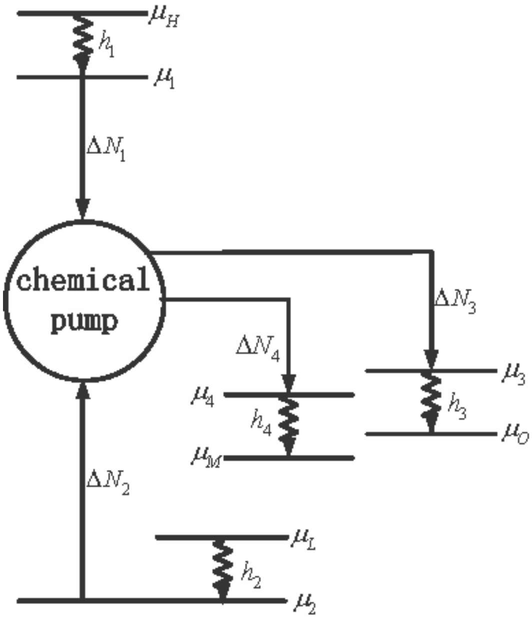

Figure 1. Model of an isothermal endoreversible four-mass-reservoir chemical pump

3. Fundamental optimal relation

According to the laws of mass and energy conservations, one has

$$\Delta N_1 + \Delta N_2 - \Delta N_3 - \Delta N_4 = 0 \tag{3}$$

$$\mu_1 \Delta N_1 + \mu_2 \Delta N_2 - \mu_3 \Delta N_3 - \mu_4 \Delta N_4 = 0 \tag{4}$$

Defining a parameter a denotes the ratio of the transferred energy of the fourth mass-reservoir to the total transferred energy of the third and the fourth mass-reservoirs

$$a = \mu_M \Delta N_4 / (\mu_O \Delta N_3 + \mu_M \Delta N_4) \tag{5}$$

According to the definitions of COP χ and the rate of energy pumping Σ of the chemical pump, one has

$$\chi = \frac{\mu_O \Delta N_3 + \mu_M \Delta N_4}{\mu_H \Delta N_1}, \Sigma = \frac{\mu_O \Delta N_3 + \mu_M \Delta N_4}{\tau} \tag{6}$$

Combining equations (1)-(6) gives

$$\chi = (\mu_1 - \mu_2)\mu_H{}^{-1}\{(1-a)\mu_O{}^{-1}(\mu_3 - \mu_2) + a\mu_M{}^{-1}(\mu_4 - \mu_2)\}^{-1} \tag{7}$$

$$\Sigma = [\frac{(1-a)\mu_O{}^{-1}(\mu_3-\mu_2) + a\mu_M{}^{-1}(\mu_4-\mu_2)}{h_1(\mu_1-\mu_2)(\exp\frac{\mu_H}{kT} - \exp\frac{\mu_1}{kT})} + \frac{(1-a)\mu_0{}^{-1}(\mu_1-\mu_3) + a\mu_M{}^{-1}(\mu_1-\mu_4)}{h_2(\mu_1-\mu_2)(\exp\frac{\mu_L}{kT} - \exp\frac{\mu_2}{kT})} + \frac{(1-a)\mu_O{}^{-1}}{h_3(\exp\frac{\mu_3}{kT} - \exp\frac{\mu_O}{kT})} + \frac{a\mu_M{}^{-1}}{h_4(\exp\frac{\mu_4}{kT} - \exp\frac{\mu_M}{kT})}]^{-1} \tag{8}$$

Now, the problem is to determine the optimal rate of energy pumping of the chemical pump for a given COP. Therefore, one can introduce a Lagrangian function $L = \Sigma + \lambda\chi$, where λ is the Lagrangian multiplier. One has

$$L=[\frac{(1-a)\mu_O^{-1}(\mu_3-\mu_2)+a\mu_M^{-1}(\mu_4-\mu_2)}{h_1(\mu_1-\mu_2)(\exp\frac{\mu_H}{kT}-\exp\frac{\mu_1}{kT})}+\frac{(1-a)\mu_0^{-1}(\mu_1-\mu_3)+a\mu_M^{-1}(\mu_1-\mu_4)}{h_2(\mu_1-\mu_2)(\exp\frac{\mu_L}{kT}-\exp\frac{\mu_2}{kT})}$$
$$+\frac{(1-a)\mu_O^{-1}}{h_3(\exp\frac{\mu_3}{kT}-\exp\frac{\mu_O}{kT})}+\frac{a\mu_M^{-1}}{h_4(\exp\frac{\mu_4}{kT}-\exp\frac{\mu_M}{kT})}]^{-1}+\lambda(\mu_1-\mu_2)\mu_H^{-1}\{(1-a)\mu_O^{-1}(\mu_3 \tag{9}$$
$$-\mu_2)+a\mu_M^{-1}(\mu_4-\mu_2)\}^{-1}$$

From the Euler-Lagrange equations $\partial L/\partial\mu_1=0$, $\partial L/\partial\mu_2=0$, $\partial L/\partial\mu_3=0$ and $\partial L/\partial\mu_4=0$, one can find that the following equations must be satisfied:

$$\frac{\exp\frac{\mu_1}{kT}}{h_1(\exp\frac{\mu_H}{kT}-\exp\frac{\mu_1}{kT})^2}=\frac{\exp\frac{\mu_2}{kT}}{h_2(\exp\frac{\mu_L}{kT}-\exp\frac{\mu_2}{kT})^2}=\frac{\exp\frac{\mu_3}{kT}}{h_3(\exp\frac{\mu_3}{kT}-\exp\frac{\mu_O}{kT})^2}=\frac{\exp\frac{\mu_4}{kT}}{h_4(\exp\frac{\mu_4}{kT}-\exp\frac{\mu_M}{kT})^2} \tag{10}$$

Substituting equation (10) into equations (7) and (8) yields the optimal dimensionless rate of energy pumping $\Sigma^*=\Sigma/(h_1\mu_H\exp\frac{\mu_H}{kT})$ and the COP as follows:

$$\Sigma^*=[\frac{(1-a)\mu_O^{-1}(\ln\beta-\ln\alpha)+a\mu_M^{-1}(\ln\gamma-\ln\alpha)}{[\ln(x\exp\frac{\mu_H}{kT})-\ln\alpha](1-x)\mu_H^{-1}}+\frac{b_2(1-a)\mu_H/\mu_O}{(\beta-\exp\frac{\mu_O}{kT})/\exp\frac{\mu_H}{kT}}$$
$$+\frac{b_1\{(1-a)\mu_O^{-1}[\ln(x\exp\frac{\mu_H}{kT})-\ln\beta]+a\mu_M^{-1}[\ln(x\exp\frac{\mu_H}{kT})-\ln\gamma]\}}{[\ln(x\exp\frac{\mu_H}{kT})-\ln\alpha]\mu_H^{-1}(\exp\frac{\mu_L}{kT}-\alpha)/\exp\frac{\mu_H}{kT}} \tag{11}$$
$$+\frac{b_3a\mu_H/\mu_M}{(\gamma-\exp\frac{\mu_M}{kT})/\exp\frac{\mu_H}{kT}}]^{-1}$$

$$\chi=[\ln(x\exp\frac{\mu_H}{kT})-\ln\alpha]\{(1-a)\mu_H\mu_O^{-1}(\ln\beta-\ln\alpha)+a\mu_H\mu_M^{-1}(\ln\gamma-\ln\alpha)\}^{-1} \tag{12}$$

where $x=\exp\frac{\mu_1}{kT}/\exp\frac{\mu_H}{kT}$, $b_1=h_1/h_2$, $b_2=h_1/h_3$, $b_3=h_1/h_4$,

$$\alpha=\exp\frac{\mu_2}{kT}=-\sqrt{b_1(1-x)^2x^{-1}\exp\frac{\mu_L}{kT}\exp\frac{\mu_H}{kT}+[\frac{1}{2}b_1(1-x)^2x^{-1}\exp\frac{\mu_H}{kT}]^2}+\exp\frac{\mu_L}{kT}$$
$$+\frac{1}{2}b_1(1-x)^2x^{-1}\exp\frac{\mu_H}{kT},$$

$$\beta=\exp\frac{\mu_3}{kT}=\sqrt{b_2(1-x)^2x^{-1}\exp\frac{\mu_O}{kT}\exp\frac{\mu_H}{kT}+[\frac{1}{2}b_2(1-x)^2x^{-1}\exp\frac{\mu_H}{kT}]^2}+\exp\frac{\mu_O}{kT}$$
$$+\frac{1}{2}b_2(1-x)^2x^{-1}\exp\frac{\mu_H}{kT},$$

and
$$\gamma=\exp\frac{\mu_4}{kT}=\sqrt{b_3(1-x)^2x^{-1}\exp\frac{\mu_M}{kT}\exp\frac{\mu_H}{kT}+[\frac{1}{2}b_3(1-x)^2x^{-1}\exp\frac{\mu_H}{kT}]^2}+\exp\frac{\mu_M}{kT}$$
$$+\frac{1}{2}b_3(1-x)^2x^{-1}\exp\frac{\mu_H}{kT}.$$

Eliminating $x=\exp\frac{\mu_1}{kT}/\exp\frac{\mu_H}{kT}$ from equations (11) and (12) yields the fundamental optimal relation between the dimensionless rate of energy pumping and the COP of the endoreversible four-mass-reservoir chemical pump. It can reveal the $\Sigma-\chi$ characteristics of an endoreversible chemical pump with diffusive mass transfer, as shown by solid line in Figure 2.

4. Results and discussion

(1) In order to study the characteristics of the four-mass-reservoir endoreversible chemical potential transformer, numerical examples are provided. In the calculations, $b_1=1.2$, $b_2=1$, $b_3=1.1$, $\exp\frac{\mu_L}{kT}=1.5$, $\exp\frac{\mu_L}{kT}/\exp\frac{\mu_H}{kT}=\exp(-\frac{\mu_H-\mu_L}{kT})=e^{-5}$, $\exp\frac{\mu_O}{kT}/\exp\frac{\mu_L}{kT}=\exp(\frac{\mu_O-\mu_L}{kT})=e^3$,

$\exp\frac{\mu_H}{kT}/\exp\frac{\mu_M}{kT}=\exp(\frac{\mu_H-\mu_M}{kT})=e^3$ and $T=300K$ are set. The characteristic curves between the dimensionless rate of energy pumping and the COP of four-mass-reservoir chemical pump with the diffusive mass transfer law and linear mass transfer law are shown in Figure 2. The curve with diffusive mass transfer law is shown by solid line, while the curve with linear mass transfer law is shown by dashed line. The influence of a on Σ^* versus χ characteristic is shown in Figure 3. The influence of $(\mu_O-\mu_L)/(kT)$ on Σ^* versus χ characteristic with $(\mu_H-\mu_M)/(kT)=3$ is shown in Figure 4. The influence of $(\mu_H-\mu_M)/(kT)$ on Σ^* versus χ characteristic with $(\mu_O-\mu_L)/(kT)=3$ is shown in Figure 5.

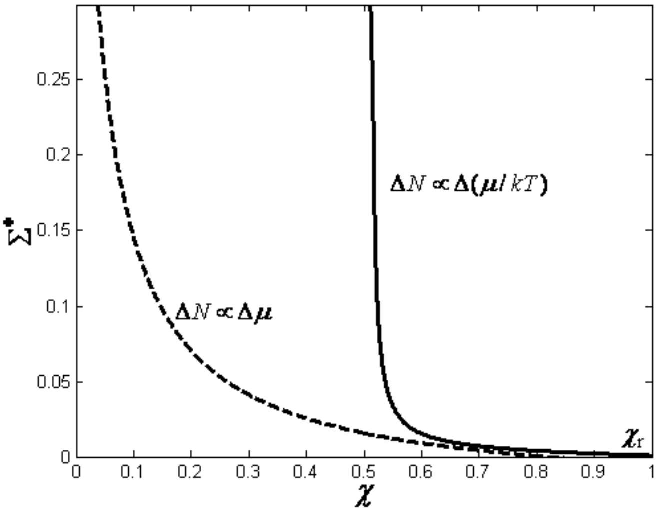

Figure 2. Relation between the optimal dimensionless rate of energy pumping and COP

It can be seen clearly from Figure 2 that the characteristic curves between the rate of energy pumping and the COP are monotonic ones. When $\Sigma=0$, one can obtain the reversible coefficient of performance χ_r of the four-mass-reservoir chemical pump, namely, $\chi_r=\dfrac{1-\mu_L/\mu_H}{1-[(1-a)/\mu_O+a/\mu_M]\mu_L}$. It can be seen that the optimal COP of the four-mass-reservoir endoreversible chemical pump can't exceed the reversible COP χ_r. This shows that the real chemical pump must decrease the COP level if one wants to obtain some rate of energy pumping.

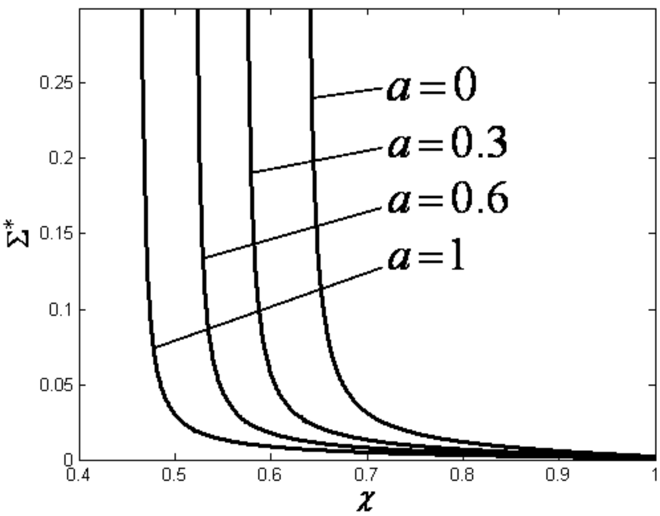

Figure 3. Influence of a on Σ^* versus χ characteristic

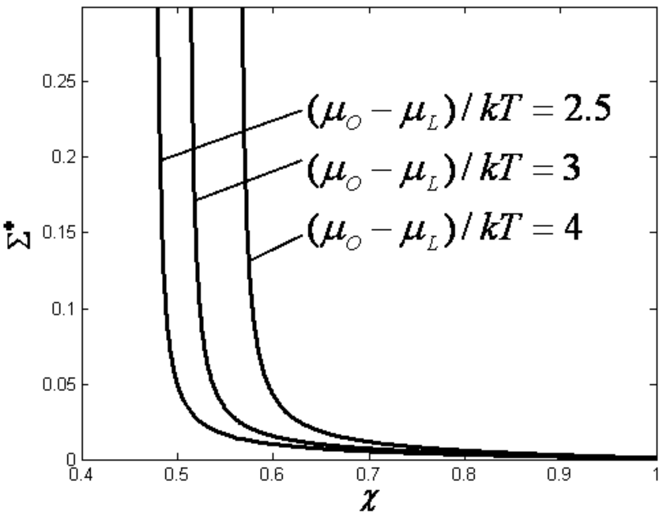

Figure 4. Influence of $(\mu_O-\mu_L)/(kT)$ on Σ^* versus χ characteristic with $(\mu_H-\mu_M)/(kT)=3$

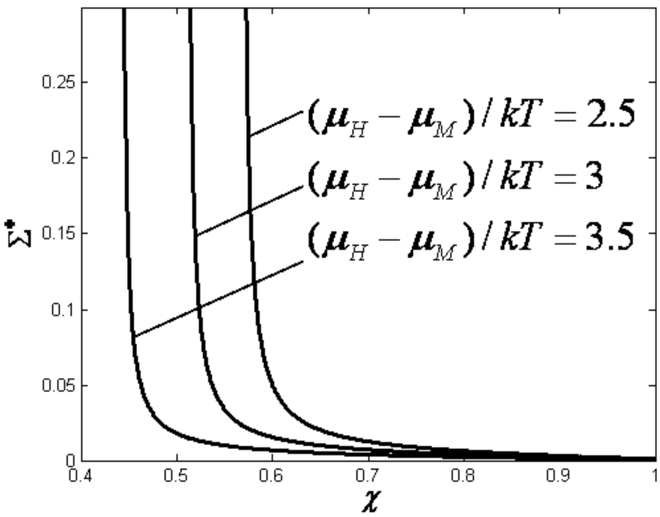

Figure 5. Influence of $(\mu_H-\mu_M)/(kT)$ on Σ^* versus χ characteristic with $(\mu_O-\mu_L)/(kT)=3$

It can be seen from Figure 3 that Σ^* decreases as a increases for the same χ. It can be seen from Figure 4 that Σ^* increases as $(\mu_O-\mu_L)/(kT)$ increases for the same χ. It can be seen from Figure 5 that Σ^* decreases as $(\mu_H-\mu_M)/(kT)$ increases for the same χ.

(2) Owing to the irreversibility of mass transfer, the entropy production rate for the cyclic system of chemical pump is larger than zero. If the environment temperature of the cyclic system is represented by T, one can obtain the minimum entropy production rate as follows:

$$\begin{aligned}\sigma &= \frac{1}{T\tau}(\mu_H\Delta N_1+\mu_L\Delta N_2-\mu_O\Delta N_3-\mu_M\Delta N_4)\\ &=\frac{\Sigma}{T}\{(1-\mu_L/\mu_H)\chi^{-1}+[(1-a)\mu_O^{-1}+a\mu_M^{-1})\mu_L-1]\}\end{aligned} \tag{13}$$

Combining equations (10) and (11) with (13), one can obtain the relation between the minimum entropy production rate and the rate of energy pumping or between the minimum entropy production rate and the COP.

(3) The cyclic model established herein can be applied to the systems such as mass exchangers, electrochemical, photochemical and solid state devices, and the fuel pumps for solar energy conversion

systems [38]. It should be pointed out that, in general, the related quantities here have different definition forms for different systems. For example, in solid-state devices, equation (2) is referred to as the current-voltage relations, where dN/dt is the current, and $\Delta\mu$ is the voltage, and in electrochemical devices, $\Delta\mu$ represents the gradient of electrochemical potential and the conjugated flow is the transport of ions. When the transferred working mediums in a chemical pump are electrons or ions, ΔN is the transferred electric charge, $\Delta\mu$ is EMF and h^{-1} is the resistance. Generally, h^{-1} is the mass flow resistance. Moreover, the working medium in a chemical pump may be gas or liquid molecules in mass exchangers in addition to a current of electrons in solid-state devices [21, 22]. The results obtained herein can provide some new theoretical instructions for the optimal design of these devices.
(4) It should be pointed out that the constitutive laws for the four chemical product conductors will be expressed not in terms of the chemical potentials μ but in terms of the more common concentration n. Both variables can be interchanged, according to the Nernst equation [18], i.e.

$$\mu = \mu_0 + kT_0 \log(n/n_0) \tag{14}$$

where μ_0 denotes the chemical potential at standard concentration n_0. Similarly, other variables, such as activity, may be introduced to replace the chemical potential with the help of some relevant relations in thermodynamics [39].

5. Conclusion

The performance of the isothermal endoreversible four-mass-reservoir chemical pump with diffusive mass transfer law is analyzed and optimized by using finite-time thermodynamics in this paper. The optimal relation between the rate of energy pumping and the COP of the endoreversible chemical pump is derived. It can be found that the optimal relation of the endoreversible four-mass-reservoir chemical pump with diffusive mass transfer law is similar as that of chemical pump with linear mass transfer law. But with numerical examples, one can find that the endoreversible four-mass-reservoir chemical pump that is governed by diffusive mass law is inherently more efficient than that governed by linear mass law. The optimally operating regions are also analyzed. Moreover, the relation between the minimum entropy production rate and the rate of energy pumping is obtained. The results obtained herein may be used in the design of mass exchangers, electrochemical, photochemical and solid state devices, fuel pumps and so on. They can provide some new theoretical instructions for the optimal design of these devices.

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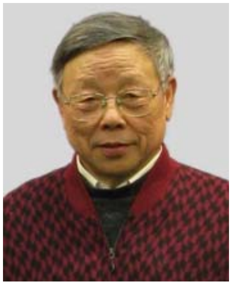

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