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Entransy dissipation minimization for one-way isothermal mass transfer processes with a generalized mass transfer law

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Abstract A class of one-way isothermal mass transfer processes is investigated in this paper. Based on the definition of mass entransy, the entransy dissipation function, which reflects the irreversibility of the mass transfer ability loss, is derived. The optimality condition for the minimum entransy dissipation of the mass transfer process with a generalized mass transfer law is obtained by applying an optimal control theory. Special cases for the linear [$g \propto \Delta(\mu)$] and the diffusive [$g \propto \Delta(c)$] mass transfer laws are obtained based on the general optimization results. The obtained results are also compared with strategies of minimum entropy generation, constant concentration ratio and constant concentration difference operations. The results obtained herein can provide some theoretical guidelines for optimal design and operation of practical mass transfer processes.

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1. Introduction

There are two standard problems in finite time thermodynamics: one is to determine the objective function limits and the relations between objective functions for the given thermodynamic system, and another is to determine the optimal thermodynamic process for given optimization objectives [1–11]. The latter belongs to functional extremum problems and needs to use the optimal control theory. It not only shows the physical limits of the optimization objectives, but also indicates the regulations or principles that the system should follow to achieve the predefined optimum objective. Thus, its significance is much more important for theoretical research and practical engineering applications. Bejan [12] first analyzed least combined entropy generation [13,14] induced by heat transfer and fluid viscosity as an objective function to optimize the geometry of heat transfer tubes and to find optimum parameters for heat exchangers. Berry et al. [3], Linetskii and Tsirlin [15], and

Andresen and Gordon [16,17] showed that the temperature ratio between high and low-temperature sides for minimum entropy generation of the heat transfer process, using the Newtonian heat transfer law [$q \propto \Delta(T)$], is a constant [3,15,16], and further investigated optimal paths for minimum entropy generation of heat transfer processes with the generalized radiative heat transfer law [$q \propto \Delta(T^n)$] [17]. Based on [16,17], Badescu [18,19] further optimized heat transfer processes for the minimum lost available work by choosing a high-temperature heat bath as the reference environment. Irreversible thermodynamics attribute various transfer processes to the results of generalized forces, pushing corresponding generalized fluxes, e.g., the driving force of heat flux q is the reciprocal temperature difference, $\Delta(1/T)$, and that of the mass flux, g , is the chemical potential difference, $\Delta\mu$. The transfer processes produce dissipation inevitably, and entropy generation is the physical quantity used to measure the irreversibility of various transfer processes, which is equal to the scalar product of various transfer fluxes and the corresponding driving forces. Based on the theory of irreversible thermodynamics, Nummedal and Kjelstrup [20] showed that the reciprocal temperature difference between high and low temperature sides for the minimum entropy generation of the heat exchange process is a constant, and demonstrated the principle of Equipartition of Forces (EoF) for optimizing heat exchange processes. Based on [20], Johannessen et al. [21] further showed that the heat exchange strategy of the constant entropy generation rate operation produces

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less entropy generation than that of constant reciprocal temperature difference operations, i.e. the principle of Equipartition of Entropy Production (EoEP) is superior to that of the Equipartition of Forces (EoF). For the classical Fourier's heat transfer law, the driving force of the heat flux is the temperature difference, i.e., heat transfer obeys Newtonian heat transfer law. Balkan [22,23] showed that the principle of EoEP coincides with the heat exchange strategy of constant temperature ratio between high and low temperature sides of heat transfer processes using Newtonian heat transfer law [22], and further applied it to optimize heat exchangers with variable heat transfer coefficients [23]. Chen et al. [24] and Xia et al. [25] derived optimal paths of heat transfer processes with a generalized heat transfer law $[q \propto (\Delta(T^n))^m]$ for minimum entropy generation [24] and minimum lost available work [25], respectively, and showed that the principle of EoEP is not only valid for Newtonian and linear phenomenological heat transfer laws but also valid for the heat transfer law $[q \propto (\Delta(T^{-1}))^m]$. In real energy transfer and conversion processes, the heat and mass transfer processes always occur together. Berry et al. [3] and Tsirlin et al. [26–32] showed that the chemical potential difference for the minimum entropy generation of a one-way isothermal mass transfer process using the linear mass transfer law $[g \propto \Delta(\mu)]$ (where $\Delta(\mu)$ is the chemical potential difference) is a constant [3,26,27], and further extended this result to optimization research of heat-driven and mechanical separations [28–30], optimal separation sequences for multi-component mixtures [31] and binary distillation separation processes [32].

The irreversibility of heat/mass transfer processes is usually characterized by entropy generation. However, the entropy generation extremum is sometimes inconsistent with the best performance of the heat transfer process. From the viewpoint of thermodynamics, the performance of a heat exchanger should be better for a smaller entropy generation number, i.e. smaller heat transfer irreversibility. However, analyses of a balanced counter-flow heat exchanger by Bejan [33,34] showed that the entropy generation number increased firstly and then decreased with an increase in effectiveness. The phenomenon is often referred to as the "entropy generation paradox" [33,34]. Both Xu et al. [35] and Hesselgreaves [36] put forward different methods of modifying entropy generation numbers to avoid the 'entropy generation paradox'. Shah and Skiepko [37] analyzed the relationship between the heat exchanger effectiveness and entropy generation for 18 kinds of heat exchanger. It was found that heat exchanger effectiveness can be maximum, intermediate or minimum at maximum entropy generation. Therefore, the minimum principle of entropy generation is not always applicable to heat exchange analysis.

Guo et al. [38,39] introduced a new quantity called entransy, which corresponds to electrical potential energy in a capacitor based on the analogy between electrical and thermal systems, and put forward the extremum principle of entransy dissipation for optimizing heat transfer processes. The entransy dissipation extremum principle (i.e. the least dissipation of heat transport potential capacity in [40]) was applied to optimize the volume-to-point access thermal conduction problem in [40]. With a fixed volume-averaged conductivity as the constraint, an optimized thermal conductivity distribution was obtained that greatly reduced the average temperature. Besides, the method of entransy dissipation minimization is used to optimize performances of various thermal systems [41–47]. Liu et al. [48–50] and Guo et al. [51] put forward the effectiveness-thermal resistance method for heat exchanger design and analysis, based on entransy dissipation [40,50,51], and discussed

the applicability of the extremum principles of entropy generation and entransy dissipation for heat exchanger optimization [49,51]. The monotonic decrease of effectiveness by increasing thermal resistance [51] showed that the heat exchanger irreversibility could be described by its entransy dissipation-based thermal resistance when evaluated from the transport process viewpoint, while the so-called entropy generation paradox occurred, if the irreversibility was measured by the entropy generation number for a heat exchanger. Xia et al. [52,53] showed that the temperature difference for the minimum entransy dissipation of the heat exchange process using Newtonian heat transfer law is a constant [52,53], and the temperature ratio for the linear phenomenological heat transfer law is a constant [53]. Xia et al. [54] further optimized the liquid–solid phase change processes for minimum entransy dissipation. Chen et al. [55] optimized the heat transfer in a thermal network with two heat exchangers, and found that maximum entransy dissipation corresponds to the maximum heat transfer rate with prescribed wall temperatures of the heat exchangers, while the minimum entropy generation does not.

Based on the analogy between heat- and mass-transfer processes, Chen et al. [56–60] defined a mass entransy and put forward the extremum principle of mass entransy dissipation (i.e. dissipation of the mass transport potential capacity in [56]) for optimizing mass transfer processes, such as laminar flow mass transfer [56], photocatalytic oxidation reactors [57], decontamination ventilation design in space station cabins [58] and evaporative cooling systems [59,60]. Xia et al. [61] investigated the minimum entransy dissipation of the one-way isothermal mass transfer process with the diffusive mass transfer law $[g \propto \Delta(c)]$ (where $\Delta(c)$ is the concentration difference). Yuan and Chen [62] further investigated the applicability of the two optimization criteria of the maximum exergy efficiency method and the minimum entransy dissipation-based thermal resistance method in flow and area distribution optimizations for evaporative cooling systems, and found that when the entransy dissipation-based thermal resistance reaches a minimum, the cooling capacity of the system reaches a maximum, i.e. the optimal evaporative cooling performance, but the exergy efficiency does not achieve its maximum value at the same time. Based on [3,26–32,56–62], this paper will further investigate the one-way isothermal mass transfer process with a generalized mass transfer law. The optimality condition for the minimum entransy dissipation of mass transfer processes will be obtained by applying the optimal control theory, and the effects of heat transfer laws will be also analyzed.

2. Physical model

Figure 1 shows a model of the one-way isothermal mass transfer process. Both mixtures, at high and low concentration sides, are binary. In order to distinguish the component that participates in the mass transfer process from that which does not (e.g. the mixture passes through a semi-permeable membrane), the component that participates in the mass transfer process is called the key component, while the other is called the inert component. Attention should be paid to the fact that the components in the mixtures are classified into two species, only according to whether the component participates in the mass transfer process or not, which is independent of the detailed number of components in the mixture. So, the results obtained in this paper are also valid for cases in which the number of components is three or more. The contact surface between the two mixtures only allows

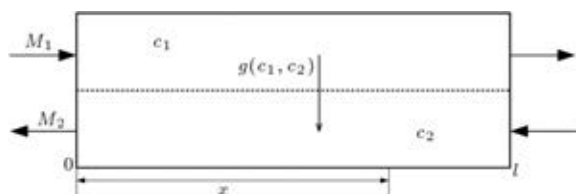


Figure 1: Model of one-way isothermal mass transfer process.

the key component to pass. c_1 and c_2 ($c_1 > c_2$) are the key component concentrations (expressed as the mass fraction or mole fraction) corresponding to the mixtures at high and low concentration sides, respectively. m_1 and m_2 are the amount of flux rate (expressed as the mass flux rate or mole flux rate) of the key components, and M_1 and M_2 are the total amount of flux rates (expressed as the mass flux rate or mole flux rate) of the mixtures. l is the total length of the mass transfer equipment. The mass transfer flux rate between the high and low concentration sides is g , which satisfies the relation, $g = -dm_1/dx = dm_2/dx$.

According to [56–62], the mass entransy, E , of the key component is given by:

$$E = \frac{1}{2}mc = \frac{1}{2}Mc^2, \quad (1)$$

where c is the key component concentration in the mixture. When the concentration, c , is expressed as the mass fraction, m and M are the mass of the key component in the mixture and the total mass of the mixture, respectively. When the concentration, c , is expressed as the mole fraction, m and M are the mole numbers of the key component in the mixture and the total mole number of the mixture, respectively. The mole mass of the key component only depends on its physical characteristic, so the expression of the mass fraction is equivalent to that of the mole fraction. The mass entransy, E , could be used to represent the ability of the key component in a mixture to transfer the mass to the outside. From Eq. (1), one further obtains the change of the mass entransy, E , as follows:

$$dE = d\left(\frac{1}{2}mc\right) = \frac{1}{2}m dc + \frac{1}{2}c dm, \quad (2)$$

where the first term on the right side of the second equal sign is the change of mass entransy due to the change in the key component concentration, and the second term on the right side of the second equal sign is the change of mass entransy due to the change in the amount of the key component. The mixture consists of two parts, the key component and the inert component. By allowing the amount of the inert component in the mixture be \tilde{m} , one further obtains:

$$\tilde{m} = M(1 - c) = m(1 - c)/c. \quad (3)$$

Eq. (3) further gives:

$$m = \frac{\tilde{m}c}{(1 - c)}. \quad (4)$$

Differentiating Eq. (4) with respect to concentration, c , yields:

$$dm = \frac{\tilde{m}dc}{(1 - c)^2}. \quad (5)$$

Substituting Eqs. (4) and (5) into Eq. (2) yields:

$$dE = \left(c - \frac{c^2}{2}\right) dm. \quad (6)$$

From Eq. (6), one further obtains the entransy balance equations corresponding to the high and low concentration sides of the mass transfer process, respectively, as follows:

$$E_{1,\text{inl}} - E_{1,\text{out}} = \frac{1}{2}m_{1,\text{inl}}c_{1,\text{inl}} - \frac{1}{2}m_{1,\text{out}}c_{1,\text{out}} = \int_0^l \left[g \left(c_1 - \frac{c_1^2}{2} \right) \right] dx, \quad (7)$$

$$E_{2,\text{inl}} - E_{2,\text{out}} = \frac{1}{2}m_{2,\text{inl}}c_{2,\text{inl}} - \frac{1}{2}m_{2,\text{out}}c_{2,\text{out}} = \int_0^l \left[-g \left(c_2 - \frac{c_2^2}{2} \right) \right] dx. \quad (8)$$

Adding Eq. (7) to Eq. (8) yields:

$$(E_{1,\text{inl}} + E_{2,\text{inl}}) - (E_{1,\text{out}} + E_{2,\text{out}}) = E_{\text{inl}} - E_{\text{out}} = \Delta E = \int_0^l \left[h(c_1 - c_2)^2 \left(1 - \frac{c_1 + c_2}{2} \right) \right] dx. \quad (9)$$

Eq. (9) shows that the total entransy flux, E_{out} , of the high and low concentration side mixtures at the outlet is smaller than that at the inlet, and the difference between them is called the entransy dissipation function, ΔE , of the one-way isothermal mass transfer process.

Analogous to the equivalent thermal resistance, $R_E = \Delta E/Q^2$, based on thermal entransy dissipation during heat transfer processes [38–53], where Q is the amount of heat transfer, the equivalent mass resistance, R_E , based on the mass entransy dissipation function, ΔE , during the mass transfer process, is:

$$R_E = \frac{\Delta E}{N^2} = \frac{\int_0^l h(c_1 - c_2)^2 \left(1 - \frac{c_1 + c_2}{2} \right) dx}{\left[\int_0^l h(c_1 - c_2) dx \right]^2}, \quad (10)$$

where N is the total amount of transferred material per unit time during the mass transfer process. The entransy dissipation extremum principle for mass transfer processes [56–62] states that maximum entransy dissipation leads to maximum mass flux at given boundary concentrations, while minimum entransy dissipation leads to minimum concentration difference at the given boundary mass flux. Both could be reduced to the principle of minimum mass resistance, so that R_E of Eq. (10) measures the effectiveness of the mass transfer process. The smaller R_E is, the better the effectiveness of the mass transfer process is. From Eq. (10), optimizing the mass transfer process with the objective of minimum ΔE is equivalent to that with the objective of minimum R_E when the total mass transfer amount, N , is fixed. For the one-way mass transfer process, as shown in Figure 1, i.e. there is a transfer of the key component only between two fluxes, one obtains:

$$\frac{dM_1}{dx} = \frac{dm_1}{dx} = -g(c_1, c_2). \quad (11)$$

Combining Eq. (5) with Eq. (11) yields:

$$\frac{dc_1}{dx} = -\frac{h(1 - c_1)^2(c_1 - c_2)}{\tilde{m}_1}, \quad (12)$$

where \tilde{m}_1 is the amount of flux rate of the inert component at the high-concentration side.

3. Average optimal control optimization

The problem now is to determine the optimal distributions of the key component concentrations, c_1 and c_2 , corresponding to the high and low concentration sides for minimizing

ΔE of Eq. (9), subject to the constraint of Eq. (12). Apparently, this functional extremum is a typical optimal control problem. One could solve Euler–Lagrange equations for optimal solutions by constructing a modified Lagrange function. Tsirlin et al. [27,63–65] and Mironova et al. [66] developed a more powerful optimization method introduced into thermodynamics, i.e. averaged optimal control. The traditional theory requires specification of the behavior of the system at every point in time along the process. Averaged optimal control relaxes that requirement and is satisfied fixing these quantities, on average, for the process as a whole. For the peculiarity of the optimization problem considered herein and according to [3,27,63–66], the solving process can be simplified by transforming this optimal control problem to a class of averaged optimal control problems. It follows from Eq. (12) that:

$$\int_{c_{1,\text{out}}}^{c_{1,\text{inl}}} \frac{\tilde{m}_1}{g(c_1, c_2)(1 - c_1)^2} dc_1 = l. \quad (13)$$

Substituting Eq. (12) into Eq. (9) yields:

$$\Delta E = \int_{c_{1,\text{out}}}^{c_{1,\text{inl}}} \left[(c_1 - c_2) \left(1 - \frac{c_1 + c_2}{2} \right) \frac{\tilde{m}_1}{(1 - c_1)^2} \right] dc_1. \quad (14)$$

The problem now is to determine the minimum value of Eq. (14) subject to the constraint of Eq. (13). The modified Lagrangian, L , is given by:

$$L = \frac{\tilde{m}_1}{(1 - c_1)^2} \left[(c_1 - c_2) \left(1 - \frac{c_1 + c_2}{2} \right) + \frac{\lambda}{g(c_1, c_2)} \right], \quad (15)$$

where λ is the Lagrangian multiplier, which is a constant to be determined. From the extreme condition, $\partial L / \partial c_2 = 0$, one can obtain:

$$g^2(c_1, c_2)(c_2 - 1) = \lambda \frac{\partial g}{\partial c_2}. \quad (16)$$

Eq. (16) is the optimality condition for the minimum entransy dissipation of the mass transfer process. For the given mass transfer law, $g(c_1, c_2)$, the optimal, $c_1(x)$ and $c_2(x)$, are obtained by combining Eqs. (12) with (16).

4. Special cases and other mass transfer strategies

The authors of [3,26,27] optimized the one-way isothermal mass transfer process for minimum entropy generation with linear [$g \propto \Delta(\mu)$] and diffusive [$g \propto \Delta(c)$] mass transfer laws. Besides the strategies of minimum entransy dissipation ($\Delta E = \min$) and minimum entropy generation ($\Delta S = \min$), there may be other mass transfer strategies in real mass transfer processes, such as the strategies of constant concentration difference ($c_1 - c_2 = \text{const}$) and constant concentration ratio ($c_1/c_2 = \text{const}$). For research on thermodynamic optimization, people always attributed various research results to some simple optimization principles that could provide effective theoretical guidelines for practical thermodynamic processes, such as Equipartition of Forces (EoF) [20], Equipartition of Entropy Production (EoEP) [21,23], Equipartition of Temperature Difference (EoTD) [22] and so on. For the diffusive mass transfer law [$g \propto \Delta(c)$], the driving force of the mass flux, g , is the concentration difference, $\Delta(c)$. Thus, the mass transfer strategy of $c_1 - c_2 = \text{const}$ is equivalent to the principle of EoF corresponding to the diffusive mass transfer law. Similarly, the driving force of the mass flux, g , for the linear mass transfer law [$g \propto \Delta(\mu)$] is the chemical potential difference, $\Delta(\mu)$, while the chemical potential, μ , of the component in the mixture and its concentration, c ,

satisfy the relation, $\mu = \mu_0 + RT \ln c$, where μ_0 is the standard chemical potential of the component, and R and T are the universal gas constant and the temperature, respectively. So, the strategy of $c_1/c_2 = \text{const}$ is equivalent to that of $\mu_1 - \mu_2 = \text{const}$, i.e., the principle of EoF corresponding to the linear mass transfer law. The cases with linear and the diffusive mass transfer laws will be analyzed in the following sections, respectively.

4.1. Linear mass transfer law [$g \propto \Delta(\mu)$]

4.1.1. The strategy of the minimum entransy dissipation

When the mass transfer process obeys the linear mass transfer law in linear irreversible thermodynamics, one obtains:

$$g(c_1, c_2) = h_\mu(\mu_1 - \mu_2) = h_\mu RT \ln(c_1/c_2), \quad (17)$$

where h_μ is the phenomenological mass transfer coefficient. Substituting Eq. (17) into Eq. (16) yields:

$$c_2(1 - c_2)[\ln(c_1/c_2)]^2 = \lambda / (h_\mu RT). \quad (18)$$

Eq. (18) further gives:

$$c_1 = c_2 \exp \left(\sqrt{\frac{\lambda}{h_\mu RT c_2 (1 - c_2)}} \right). \quad (19)$$

Differentiating Eq. (19) with respect to x yields:

$$\frac{dc_1}{dx} = \exp \left(\sqrt{\frac{\lambda}{h_\mu RT c_2 (1 - c_2)}} \right) \times \left[1 + \frac{(2c_2 - 1)}{2c_2^{1/2}} (1 - c_2)^{3/2} \sqrt{\frac{\lambda}{h_\mu RT}} \right] \frac{dc_2}{dx}. \quad (20)$$

Substituting Eqs. (19) and (20) into Eq. (12) yields:

$$\frac{dc_2}{dx} = - \frac{h_\mu RT \sqrt{\frac{\lambda}{h_\mu RT c_2 (1 - c_2)}} \left[1 - c_2 \exp \left(\sqrt{\frac{\lambda}{h_\mu RT c_2 (1 - c_2)}} \right) \right]^2}{\tilde{m}_1 \exp \left(\sqrt{\frac{\lambda}{h_\mu RT c_2 (1 - c_2)}} \right) \left[1 + \frac{(2c_2 - 1)}{2c_2^{1/2} (1 - c_2)^{3/2}} \sqrt{\frac{\lambda}{h_\mu RT}} \right]}. \quad (21)$$

From the known boundary conditions, $c_1(0) = c_{1,\text{inl}}$ and $c_1(l) = c_{1,\text{out}}$, the unknown constant, λ , can be determined by combining Eq. (19) with Eq. (21), and, then, $c_1(x)$ and $c_2(x)$ are further obtained. The minimum entransy dissipation, ΔE_{min} , of the mass transfer process is obtained by substituting $c_1(x)$ and $c_2(x)$ into Eq. (9) and integrating it numerically.

4.1.2. The strategy of the minimum entropy generation

The entropy generation of the mass transfer process is:

$$\Delta S = \int_0^l \frac{g(c_1, c_2)[\mu_1(c_1) - \mu_2(c_2)]}{T} dx, \quad (22)$$

where $\mu_1(c_1)$ and $\mu_2(c_2)$ are the chemical potentials of the key component corresponding to high and low concentration sides. According to [3,26,27], the chemical potential difference of the key component between the high and low concentration sides for minimum entropy generation is a constant, i.e. the mass flux rate, g , of the mass transfer process or the concentration ratio, c_1/c_2 , is a constant as follows:

$$\mu_1 - \mu_2 = RT \ln(c_1/c_2) = a, \quad (23)$$

where a is an integration constant to be determined. Substituting Eq. (23) into Eq. (12) yields:

$$\frac{dc_1}{dx} = -\frac{h_\mu a(1-c_1)^2}{\tilde{m}_1} \quad (24)$$

The boundary conditions, $c_1(0) = c_{1,\text{inl}}$ and $c_1(l) = c_{1,\text{out}}$, are known. From Eq. (24), the integration constants, a and $c_1(x)$, respectively, are obtained as follows:

$$a = \frac{\tilde{m}_1(c_{1,\text{inl}} - c_{1,\text{out}})}{h_\mu L(1 - c_{1,\text{inl}})(1 - c_{1,\text{out}})} \quad (25)$$

$$c_1(x) = \frac{(c_{1,\text{inl}} - c_{1,\text{out}})x - Lc_{1,\text{inl}}(1 - c_{1,\text{out}})}{(c_{1,\text{inl}} - c_{1,\text{out}})x - L(1 - c_{1,\text{out}})} \quad (26)$$

From Eqs. (23), (25) and (26), one further obtains:

$$c_2(x) = \frac{(c_{1,\text{inl}} - c_{1,\text{out}})x - Lc_{1,\text{inl}}(1 - c_{1,\text{out}})}{(c_{1,\text{inl}} - c_{1,\text{out}})x - L(1 - c_{1,\text{out}})} \times \exp\left[\frac{h_\mu RTL(1 - c_{1,\text{inl}})(1 - c_{1,\text{out}})}{\tilde{m}_1(c_{1,\text{inl}} - c_{1,\text{out}})}\right] \quad (27)$$

Substituting Eqs. (26) and (27) into Eq. (22) yields:

$$\Delta S_{\text{min}} = \frac{\tilde{m}_1^2(c_{1,\text{inl}} - c_{1,\text{out}})^2}{h_\mu LT(1 - c_{1,\text{inl}})^2(1 - c_{1,\text{out}})^2} \quad (28)$$

The entransy dissipation for minimum entropy generation of the mass transfer process with the linear mass transfer law is obtained by substituting Eqs. (26) and (27) into Eq. (9) and integrating it numerically.

4.1.3. The strategy of constant concentration difference

When the concentration difference is a constant, one obtains:

$$c_1 - c_2 = a, \quad (29)$$

where a is a constant to be determined. Substituting Eq. (29) into Eq. (12) yields:

$$\frac{dc_1}{dx} = -\frac{h_\mu RT(1-c_1)^2 \ln\left(\frac{c_1}{c_1-a}\right)}{\tilde{m}_1} \quad (30)$$

Since boundary conditions $c_1(0) = c_{1,\text{inl}}$ and $c_1(l) = c_{1,\text{out}}$ are known, the unknown constants, a and $c_1(x)$, are obtained from Eq. (30). The entransy dissipation, ΔE , of the mass transfer process is obtained by substituting $c_1(x)$ and $c_2(x)$ into Eq. (9) and integrating it numerically.

4.2. Fick's diffusive mass transfer law [$g \propto \Delta(c)$] [61]

4.2.1. The strategy of the minimum entransy dissipation

When the mass transfer process obeys Fick's diffusive mass transfer law, one obtains:

$$g = h_c(c_1 - c_2), \quad (31)$$

where h_c is the diffusive mass transfer coefficient. Eq. (16) further gives:

$$\lambda = h_c(1 - c_2)(c_1 - c_2)^2. \quad (32)$$

From Eq. (32), one can see that the optimal mass transfer strategy for minimum entransy dissipation of the mass transfer process is that the product of the square of the key component concentration difference $(c_1 - c_2)^2$ between the high and low

concentration sides and the inert component concentration, $(1 - c_2)$, at the low-concentration side, should be a constant. From Eq. (32), one further obtains:

$$c_1 = c_2 + \sqrt{\frac{\lambda}{h(1 - c_2)}} \quad (33)$$

Differentiating Eq. (33), with respect to x , yields:

$$\frac{dc_1}{dx} = \left[1 + \frac{1}{2} \sqrt{\frac{\lambda}{h(1 - c_2)^3}}\right] \frac{dc_2}{dx} \quad (34)$$

Substituting Eqs. (33) and (34) into Eq. (12) yields:

$$\frac{dc_2}{dx} = -\frac{h}{\tilde{m}_1} \left[\left(1 - c_2 - \sqrt{\frac{\lambda}{h(1 - c_2)}}\right)^2 \times \sqrt{\frac{\lambda}{h(1 - c_2)}} \right] / \left[1 + \frac{1}{2} \sqrt{\frac{\lambda}{h(1 - c_2)^3}} \right] \quad (35)$$

Integrating Eq. (35) by using the symbol-calculation function of Matlab software yields:

$$\left. \begin{aligned} & \left. \left. \begin{aligned} & \frac{(c_2 - 1)}{(1 - c_2)^{3/2} - \sqrt{\lambda/h}} \\ & + \frac{1}{3} \frac{\ln[\sqrt{(1 - c_2)} - (\lambda/h)^{1/6}]}{(\lambda/h)^{1/6}} \\ & - \frac{1}{6} \frac{\ln[(1 - c_2) + \sqrt{(1 - c_2)}(\lambda/h)^{1/6} + (\lambda/h)^{1/3}]}{(\lambda/h)^{1/6}} \\ & + \frac{\sqrt{3} \arctan\left\{\frac{\sqrt{3}}{3} \left[\frac{2\sqrt{(1 - c_2)}}{(\lambda/h)^{1/6}} + 1\right]\right\}}{3(\lambda/h)^{1/6}} \end{aligned} \right. \right. \Bigg|_{c_{2,\text{out}}}^{c_2(x)} \\ & = \frac{\sqrt{\lambda h}}{\tilde{m}_1} x + a, \end{aligned} \right. \quad (36)$$

where a is an integration constant. From boundary conditions, $c_1(0) = c_{1,\text{inl}}$ and $c_1(l) = c_{1,\text{out}}$, constants λ and a can be determined by combining Eq. (33) with Eq. (35), and then $c_1(x)$ and $c_2(x)$ are also obtained. Finally, the minimum entransy dissipation, ΔE_{min} , of the mass transfer process is obtained by substituting $c_1(x)$ and $c_2(x)$ into Eq. (9), and then integrating it numerically.

4.2.2. The strategy of the minimum entropy generation

According to [3,26,27], the optimal relationship between concentrations $c_1(x)$ and $c_2(x)$ for minimum entropy generation of the mass transfer process, using Fick's diffusive mass transfer law, is given by:

$$c_1 = c_2 + \sqrt{ac_2}, \quad (37)$$

where a is an integration constant to be determined. From Eq. (37), one can see that the optimal mass transfer strategy for minimum entropy generation is that the ratio of the square of the key component concentration difference, $(c_1 - c_2)^2$, between the high and low concentration sides to the key component concentration, c_2 , at the low-concentration side, is a constant. Comparison between Eqs. (19) and (24) shows that the strategy of minimum entransy dissipation is significantly different from that of minimum entropy generation. Solving Eq. (37) for c_2 yields:

$$c_2 = c_1 + \frac{a}{2} - \sqrt{c_1 a + \frac{a^2}{4}} \quad (38)$$

Substituting Eq. (38) into Eq. (12) yields:

$$\frac{dc_1}{dx} = \frac{h(1-c_1)^2 \left(\frac{a}{2} - \sqrt{c_1 a + \frac{a^2}{4}} \right)}{\tilde{m}_1} \quad (39)$$

With the known boundary conditions, $c_1(0) = c_{1,\text{inl}}$ and $c_1(l) = c_{1,\text{out}}$, the unknown integration constants, a and $c_1(x)$, can be determined from Eq. (39), and then, $c_2(x)$ is obtained by substituting a and $c_1(x)$ into Eq. (38). The entransy dissipation for minimum entropy generation of the mass transfer process is obtained by substituting $c_1(x)$ and $c_2(x)$ into Eq. (9) and then integrating it numerically.

4.2.3. The strategy of constant concentration difference

When the concentration difference is a constant, i.e. $g(c_1, c_2) = \text{const}$ or $c_1(x) - c_2(x) = \text{const}$, the concentration gradient of the mass transfer process is uniform. Let $c_1 - c_2 = a$; it follows from Eq. (12) that:

$$\frac{dc_1}{dx} = -\frac{ha(1-c_1)^2}{\tilde{m}_1} \quad (40)$$

The known boundary conditions are $c_1(0) = c_{1,\text{inl}}$ and $c_1(l) = c_{1,\text{out}}$, and then a and $c_1(x)$ are obtained from Eq. (40), which are, respectively, given by:

$$a = \frac{\tilde{m}_1(c_{1,\text{inl}} - c_{1,\text{out}})}{hl(1 - c_{1,\text{inl}})(1 - c_{1,\text{out}})}, \quad (41)$$

$$c_1(x) = \frac{(c_{1,\text{out}} - c_{1,\text{inl}})(x/l) + c_{1,\text{inl}}(1 - c_{1,\text{out}})}{(c_{1,\text{out}} - c_{1,\text{inl}})(x/l) + (1 - c_{1,\text{out}})} \quad (42)$$

Since the concentrations, $c_1(x)$ and $c_2(x)$, satisfy the relation $c_1 - c_2 = a$, then $c_2(x)$ is obtained from Eqs. (41) and (42) as follows:

$$c_2(x) = \frac{(c_{1,\text{out}} - c_{1,\text{inl}})(x/l) + c_{1,\text{inl}}(1 - c_{1,\text{out}})}{(c_{1,\text{out}} - c_{1,\text{inl}})(x/l) + (1 - c_{1,\text{out}})} - \frac{\tilde{m}_1(c_{1,\text{inl}} - c_{1,\text{out}})}{hl(1 - c_{1,\text{inl}})(1 - c_{1,\text{out}})} \quad (43)$$

The entransy dissipation, ΔE , of the mass transfer process for the strategy of the constant mass transfer flux rate is obtained by substituting Eqs. (42) and (43) into Eq. (9), which is given by:

$$\Delta E = \frac{\tilde{m}_1^3(c_{1,\text{inl}} - c_{1,\text{out}})^3}{2(hl)^2(1 - c_{1,\text{inl}})^3(1 - c_{1,\text{out}})^3} - \frac{\tilde{m}_1^2(c_{1,\text{inl}} - c_{1,\text{out}})}{hl(1 - c_{1,\text{inl}})(1 - c_{1,\text{out}})} \ln \frac{(1 - c_{1,\text{inl}})}{(1 - c_{1,\text{out}})} \quad (44)$$

4.2.4. The strategy of constant concentration ratio

The concentration ratio of the key component between the high and low concentration sides is a constant, i.e. $c_1(x)/c_2(x) = \text{const}$. The chemical potential of the component in the mixture and its concentration satisfy the relation $\mu = \mu_0 + RT \ln c$. So, $c_1(x)/c_2(x) = \text{const}$ coincides with the fact that the chemical potential difference is a constant, i.e. $\Delta(\mu) = \text{const}$. Let $c_2/c_1 = a$; it follows from Eq. (12) that:

$$\frac{dc_1}{dx} = -\frac{h(1-a)(1-c_1)^2 c_1}{\tilde{m}_1} \quad (45)$$

The boundary conditions, $c_1(0) = c_{1,\text{inl}}$ and $c_1(l) = c_{1,\text{out}}$, are known, and then a and $c_1(x)$ are obtained from Eq. (45)

as follows:

$$a = \frac{\tilde{m}_1}{hl} \left\{ \ln \left[\frac{c_{1,\text{out}}(1 - c_{1,\text{inl}})}{c_{1,\text{inl}}(1 - c_{1,\text{out}})} \right] + \frac{c_{1,\text{out}} - c_{1,\text{inl}}}{(1 - c_{1,\text{out}})(1 - c_{1,\text{inl}})} \right\} + 1, \quad (46)$$

$$\begin{aligned} & \ln \frac{c_1(x)}{1 - c_1(x)} + \frac{1}{1 - c_1(x)} \\ &= \frac{x}{l} \left\{ \ln \left[\frac{c_{1,\text{out}}(1 - c_{1,\text{inl}})}{c_{1,\text{inl}}(1 - c_{1,\text{out}})} \right] + \frac{c_{1,\text{out}} - c_{1,\text{inl}}}{(1 - c_{1,\text{out}})(1 - c_{1,\text{inl}})} \right\} \\ &+ \ln \frac{c_{1,\text{inl}}}{1 - c_{1,\text{inl}}} + \frac{1}{1 - c_{1,\text{inl}}} \end{aligned} \quad (47)$$

Eq. (47) determines the concentration, $c_1(x)$, at the high concentration side versus the position, x , for the mass transfer strategy of constant concentration difference. For the given values of $c_{1,\text{inl}}$, $c_{1,\text{out}}$ and l , the concentration, $c_1(x)$, versus the position, x , can be obtained by using the nonlinear equation solving function “@fsolve” in the Matlab toolbox, and solving Eq. (47) numerically. Since $c_2(x) = ac_1(x)$, the entransy dissipation of the mass transfer process for the strategy of a constant concentration ratio is obtained by substituting $c_1(x)$ and $c_2(x)$ into Eq. (9) and integrating it numerically.

5. Numerical examples and discussions

As an illustrative example, the following calculation parameters are chosen reasonably. Assume that the mole flux rate of the inert component at the high-concentration side is $\tilde{m} = 3.6$ mol/s. The concentrations of the key component at the inlet and the outlet are $c_{1,\text{inl}} = 0.8$ and $c_{1,\text{out}} = 0.4$, respectively. The total length of the mass transfer equipment is $l = 3$ m. According to [61], the mass transfer coefficient for the diffusive mass transfer law is set to be $h_c = 20$ mol/(m s). For different mass transfer laws, the mass transfer coefficients must be changed in order to generate mass transfer rates that are comparable to each other. So, the mass transfer coefficient for the linear mass transfer law is set to be $h_\mu = 4 \times 10^{-3}$ J/(mol²·m·s). Both mass transfer coefficients are assumed to keep constant, along with the position. The mass transfer amount of the key component per unit time in the mass transfer equipment is $N = \tilde{m}_1/(1 - c_{1,\text{inl}}) - \tilde{m}_1/(1 - c_{1,\text{out}}) = 12$ mol/s. The universal gas constant is $R = 8.3145$ J/(mol·K). The temperature in the mass transfer equipment is $T = 298.15$ K. The analysis for the case with the diffusive mass transfer law was obtained in [61]. Firstly, numerical examples for the linear mass transfer law will be given herein, and then optimization results for the linear and diffusive mass transfer laws will be compared with each other.

5.1. Numerical example for the linear mass transfer law [$g \propto \Delta(\mu)$]

Figures 2 and 3 show the key component concentrations, c_1 and c_2 , versus the position, x , corresponding to the high and low concentration sides for various mass transfer strategies with the linear mass transfer law, respectively, which include three different strategies of constant concentration difference ($c_1 - c_2 = \text{const}$), the minimum entropy generation ($\Delta S = \text{min}$) and the minimum entransy dissipation ($\Delta E = \text{min}$). From Figure 2, one can see that the key component concentrations, c_1 , at the high-concentration side for various mass transfer

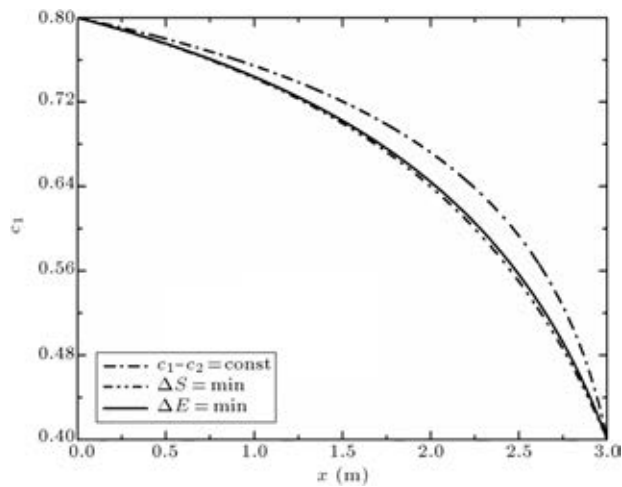


Figure 2: Key component concentration, c_1 , versus position, x , for the linear mass transfer law.

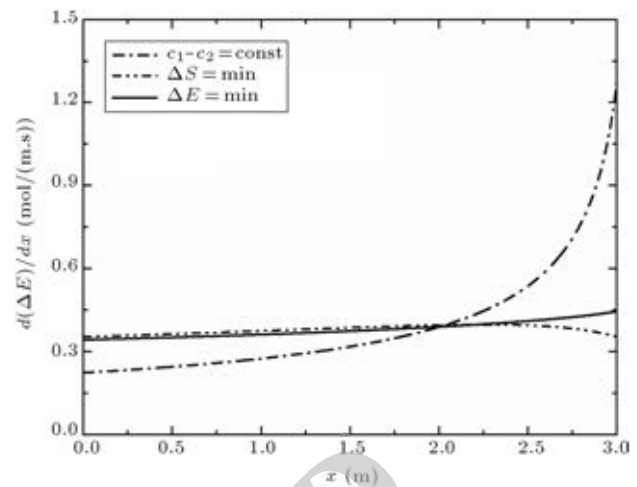


Figure 4: Entropy dissipation density, $d(\Delta E)/dx$, versus position, x , for the linear mass transfer law.

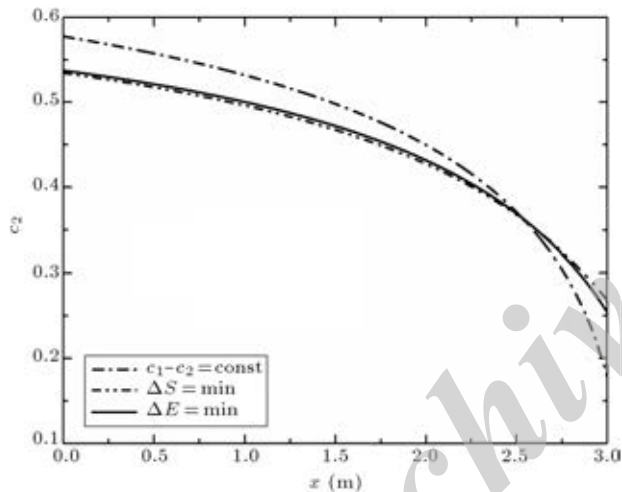


Figure 3: Key component concentration, c_2 , versus position, x , for the linear mass transfer law.

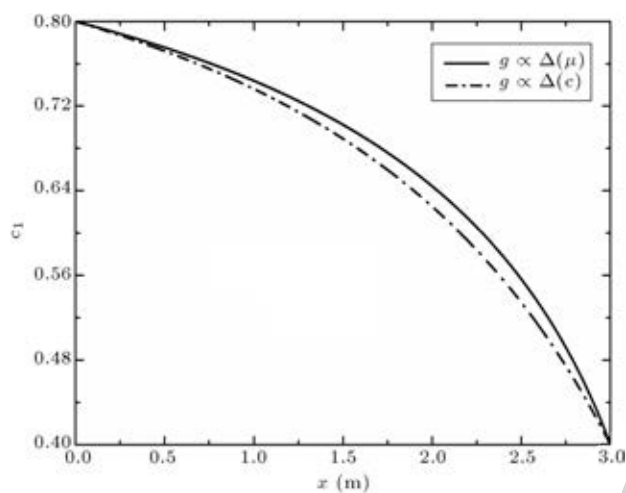
strategies decrease nonlinearly along the flow direction of the corresponding mixture. For the same position, x (except the two endpoints), the concentration, c_1 , for the strategy of $c_1 - c_2 = \text{const}$ is the highest, and the concentration, c_1 , for the strategy of $\Delta S = \text{min}$ is slightly lower than that for the strategy of $\Delta E = \text{min}$. This shows that the key component concentrations versus the position, x , corresponding to the high-concentration sides, for various mass transfer strategies, are significantly different from each other. From Figure 3, one can see that the key component concentrations, c_2 , at the low-concentration side, for various mass transfer strategies, increase nonlinearly along the flow direction of the corresponding mixture; both initial and final concentrations (i.e. $c_{1,\text{inl}}$ and $c_{1,\text{out}}$) for different mass transfer strategies are equal (the strategy of $\Delta S = \text{min}$ is the same as that of $c_1/c_2 = \text{const}$, and $c_1/c_2 > 1$). So, at the inlet of the mixture (where concentration $c_{1,\text{out}}$ at the high concentration side is relative lower), the concentration, $c_{2,\text{inl}}$, for the strategy of $\Delta S = \text{min}$ is slightly higher than that for the strategy of $\Delta E = \text{min}$, and both of them are higher than

that for the strategy of $c_1 - c_2 = \text{const}$. At the outlet of the mixture (where concentration $c_{1,\text{inl}}$ at the high concentration side is relative higher), the concentration, $c_{2,\text{out}}$, for the strategy of $\Delta E = \text{min}$ is slightly higher than that for the strategy of $\Delta S = \text{min}$; both of them are lower than that for the strategy of $c_1 - c_2 = \text{const}$. Figure 4 shows the entropy dissipation density, $d(\Delta E)/dx$, of the mass transfer process versus the position, x , for various mass transfer strategies. From Figure 4, one can see that with an increase in the position x , $d(\Delta E)/dx$ for the strategies of $c_1 - c_2 = \text{const}$ and $\Delta E = \text{min}$ increases and $d(\Delta E)/dx$, for the strategy of $\Delta S = \text{min}$, increases firstly and then decreases. Compared to the mass transfer strategy of $c_1 - c_2 = \text{const}$, the distributions of $d(\Delta E)/dx$ for the strategies of both $\Delta S = \text{min}$ and $\Delta E = \text{min}$ along position x are relatively uniformly. The more uniform the distribution of the local mass entropy dissipation rate along the position is, the smaller the entropy dissipation rates, ΔE , of the mass transfer process are, and the better the mass transfer effectiveness is.

Table 1 lists the calculation results of the key parameters for mass transfer processes, with various mass transfer strategies. For the case with the linear mass transfer law [$g \propto \Delta(\mu)$], the driving force of the mass flux, g , is the chemical potential difference, $\Delta(\mu)$. When the minimum entropy generation is chosen to be the evaluation criterion, the strategy of $\Delta S = \text{min}$ coincides with that of $c_1/c_2 = \text{const}$ or $\Delta(\mu) = \text{const}$ (i.e. the principle of EoF), and the entropy generation for the strategy of $\Delta E = \text{min}$ is closer to that for the strategy of $\Delta S = \text{min}$ compared to the strategy of $c_1 - c_2 = \text{const}$. When the minimum entropy dissipation is chosen to be the evaluation criterion, the entropy dissipation for the strategy of $\Delta S = \text{min}$ is closer to that for the strategy of $\Delta E = \text{min}$ compared to the strategy of $c_1 - c_2 = \text{const}$. Since the strategy of $\Delta S = \text{min}$ coincides with the strategy of $\Delta(\mu) = \text{const}$ (or $c_1/c_2 = \text{const}$), this shows that the principle of EoF is closer to the optimal strategy of the minimum entropy dissipation, i.e. the principle of EoF ($\Delta(\mu) = \text{const}$) is superior to the strategy of $c_1 - c_2 = \text{const}$. According to [61], when the minimum entropy dissipation is chosen to be the evaluation criterion, the strategy of $c_1 - c_2 = \text{const}$ is superior to that of $\Delta(\mu) = \text{const}$ for the mass transfer process with the diffusive mass transfer law. This also shows that the principle of constant driving force is closer to the optimal strategy of the minimum entropy dissipation.

Table 1: Calculation results of key parameters for various mass transfer strategies.

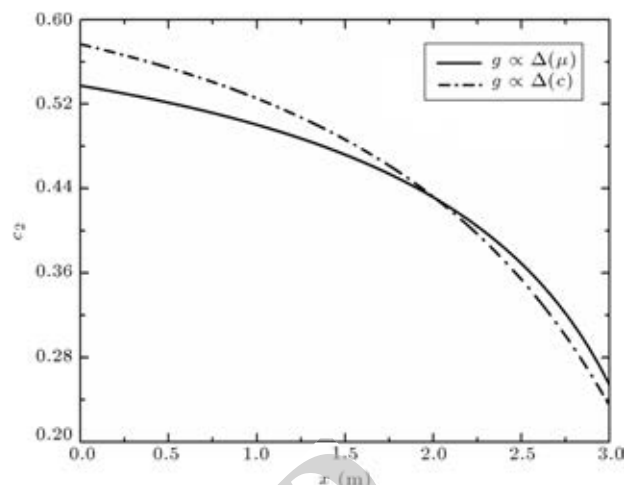
Case	$c_{2,inl}$	$c_{2,outl}$	\dot{m}_2 (mol/s)	ΔS (W/K)	ΔE (mol/s)
Linear mass transfer law [$g \propto \Delta(\mu)$]					
$c_1 - c_2 = \text{const}$	0.1775	0.5755	13.8120	42.3641	1.1781
$\Delta S = \text{min}$	0.2672	0.5344	9.3994	40.2482	1.1395
$\Delta E = \text{min}$	0.2536	0.5375	9.8693	40.3038	1.1392
Diffusive mass transfer law [$g \propto \Delta(c)$] [61]					
$c_1/c_2 = \text{const}$	0.2770	0.5539	10.3039	35.8949	1.0356
$c_1 - c_2 = \text{const}$	0.2000	0.6000	15.0000	36.2543	1.0310
$\Delta S = \text{min}$	0.2512	0.5749	12.1999	35.5925	1.0224
$\Delta E = \text{min}$	0.2339	0.5767	12.6830	35.6639	1.0218

Figure 5: Optimal key component concentration, c_1 , versus position, x , for different mass transfer laws.

5.2. Comparison of optimization results between different mass transfer laws

Figures 5 and 6 show the key component concentrations, c_1 and c_2 , versus position, x , corresponding to the high and low concentration sides for the minimum entransy dissipation of the mass transfer process with two different mass transfer laws. From Figure 5, one can see that the key component concentration, c_1 , for the linear mass transfer law is larger than that for the diffusive mass transfer law (except the two endpoints). From Figure 6, one can see that at the inlet of the mixture, the key component concentration, $c_{2,inl}$, for the linear mass transfer law is higher than that for the diffusive mass transfer law and at the outlet of the mixture, the key component concentration, $c_{2,outl}$, for the diffusive mass transfer law is higher than that for the linear mass transfer law. It is evident that the optimal key component concentrations, c_1 and c_2 , versus position x for the minimum entransy dissipation of the mass transfer process with different mass transfer laws are significantly different from each other. There are two reasons for this difference.

One is that the mass transfer laws are different, and the other is that the mass transfer coefficients change largely between different mass transfer laws. This shows that mass transfer laws have a significant effect on the optimal concentration configurations of the key component corresponding to the high and low concentration sides for minimum entransy dissipation. From the theory of irreversible thermodynamics, the product of the mass flux, g , of the mass transfer process and the

Figure 6: Optimal key component concentration, c_2 , versus position, x , for different mass transfer laws.

chemical potential difference, $\Delta(\mu)$, is equal to the product of the entropy generation, ΔS , of the mass transfer process and temperature, T , as shown in Eq. (22). Meanwhile, the results in Table 1 show that the entropy generation for the strategy of constant chemical potential difference ($\Delta(\mu) = \text{const}$) is smaller than that for the strategy of constant concentration difference ($\Delta c = \text{const}$). This reflects that the driving force of the mass flux for the mass transfer process characterized by the entropy is the chemical potential difference. Based on the definition of the mass entransy, E , the entransy dissipation of the mass transfer process is derived in this paper, as shown in Eq. (9). The results show that the entransy dissipation for the strategy of constant concentration difference ($\Delta c = \text{const}$) is smaller than that for the strategy of constant chemical potential difference ($\Delta\mu = \text{const}$). This reflects that the driving force of the mass flux for the mass transfer process characterized by the entransy is the concentration difference. For real mass transfer processes, application of Fick's diffusive mass transfer law [$g \propto \Delta(c)$] is much more widely used than that of the linear mass transfer law [$g \propto \Delta(\mu)$]. Meanwhile, when the mass transfer process is not involved in the energy conversion process, the optimization principle should be the minimum entransy dissipation.

6. Conclusion

On the basis of [3,26–32,56–62], this paper further investigated a class of one-way isothermal mass transfer processes. Based on the definition of mass entransy, the entransy dissipation function, which reflects the irreversibility of mass transfer ability loss, is derived. The optimality condition for the minimum entransy dissipation of the mass transfer process is derived by applying the optimal control theory. Special cases for linear [$g \propto \Delta(\mu)$] and diffusive [$g \propto \Delta(c)$] mass transfer laws are obtained based on general optimization results. The obtained results are also compared with the strategies of minimum entropy generation, constant concentration ratio and constant concentration difference operations. The results show that the optimal mass transfer strategy for the minimum entransy dissipation of the mass transfer process, with the diffusive mass transfer law, is that the product of the square of the key component concentration difference between the high and low concentration sides and the inert component concentration at the

low-concentration side is a constant, and the optimization result for the linear mass transfer law is significantly different from that for the diffusive mass transfer law. The mass transfer strategy of constant driving force operation is closer to the optimal mass transfer strategy. Entropy generation and entransy dissipation represent different physical meanings, and selection between the two optimum criteria (i.e. entropy generation minimization and entransy dissipation minimization) depends, of course, on the particular implementation of mass transfer processes. According to the Gouy–Stodola theorem [12], lost available work is directly proportional to entropy generation. When the mass transfer process is involved in the energy conversion process, and the objective is to maximize work output or minimize lost available work, such as distillation and separation processes [3,26–32], isothermal chemical engines [67–71] and so on, the optimization principle should be minimum entropy generation. When the pure mass transfer process is not involved in the energy conversion process, such as decontamination ventilation in space station cabins [58], evaporative cooling processes [59,60,62] and so on, the optimization principle should be minimum entransy dissipation (with a fixed mass-flux boundary). The results obtained in this paper can provide some theoretical guidelines for optimal design and operation of practical mass transfer processes.

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