Finite Time Thermodynamics: Limiting Performance of Diffusion Engines and Membrane Systems

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In this paper, the limiting performance of membrane systems with inhomogeneous composition is studied within the class of fixed rate processes. The problem of maintaining a nonequilibrium state in such a system using minimal power (separation problem) and the problem of extracting maximal power from such a system (diffusion engine problem) are formulated and solved. Results are obtained for diffusion engines with constant and periodic contact between the working body and the reservoirs.

1. Introduction

The problem of extracting work from a thermodynamic system that is not in equilibrium and its inverse problem of maintaining a system in a nonequilibrium state are central in thermodynamics. For a system that is not in equilibrium with respect to temperature, the first problem is solved using heat engines and the second using heat pumps. For a system that is not in equilibrium with respect to composition the second problem is solved using separation systems, where the first can be solved using diffusion engines. Membrane systems play a central role among separation systems and diffusion engines and they performances depend strongly on membranes' characteristics.

A vast literature is devoted to the applications of membrane systems as separation systems and as diffusion engines.[1−18] In this paper, we will study these systems within the framework of finite-time thermodynamics (e.g., refs 19, 20, 21), which is concerned with finding limiting performance for nonequilibrium thermodynamic systems, where processes have finite duration and the average rates of fluxes are given. Some of the best known results obtained here are the solutions to the problem of maximizing the power of a heat engine with given heat transfer coefficients; and to the problem of maximizing the efficiency of a heat engine with given power. System driven by difference in chemical potential have been also studied using finite-time thermodynamics.[26]

The problem of finding the limiting performance for a diffusion engine was first formulated in its simplest form in.[20] In this paper, we present a comprehensive study of the limiting performance for a diffusion engine within the class of fixed rate processes, paying special attention to the following questions:

1. What is the minimal amount of energy necessary for the separation of a mixture with a given composition into key products with given composition?

2. What is the maximal power and maximal efficiency of a diffusion engine?

The answers to these questions depend strongly on whether the input/feed mixture used by the engine is gaseous or liquid, as this determines the form of the chemical potentials and therefore the driving forces of the processes. For near ideal gas mixtures the chemical potential of the ith component of the mixture[22] is

$$\mu_i(T, P_i) = \mu_{i0}(T) + RT \ln P_i, \quad i = 1, ..., k$$

where P_i is the partial pressure of the ith component. After denoting the ratio of the partial pressure to the full pressure as x_i, we get

$$P_i = Px_i = P\frac{N_i}{N}, \quad i = 1, ..., k$$

and the chemical potential takes the form

$$\mu_i(T, P, x_i) = \mu_{i1}(T, P) + RT \ln x_i, \quad i = 1, ..., k \qquad (1)$$

Here $\mu_{i1}(T, P) = \mu_{i0}(T) + RT \ln P$, N is the number of moles of mixture and N_i is the number of moles of its ith component.

For a liquid the chemical potential has the same form as (1), but the potential $\mu_{i1}(T, P)$ is different. This is due to the fact[22] that the chemical potential $\mu_i(T, P, x_i)$ represents Gibbs molar energy of the ith component, while its derivative with respect to pressure is the molar volume of this component v_i. Unlike the case for a gas, the molar volume for a liquid is practically independent of pressure and is only weakly dependent on temperature. Since

$$\frac{\partial \mu_i}{\partial P} = \frac{\partial \mu_{i1}}{\partial P} = v_i$$

we get

$$\mu_i(T, P, x_i) = \mu_{i1}(T) + v_iP + RT \ln x_i, \quad i = 1,..., k \qquad (2)$$

We assume in the sequel that all processes are isothermal and that the temperatures of all subsystems are equal to T. All problems are first considered for gaseous and then for liquid mixtures. To make the results more specific, we consider liquid "saline engines" that use water-based saline solutions in the examples.

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2. Limiting Performance of Gas Separation Using Membrane Systems

Maximal Work in a Process with a Reservoir. Consider a system that includes reservoir (source with infinite capacity) with the temperature T, pressure P^0, and chemical potential μ^0 and the working body with the same temperature, volume $V > 0$ and chemical potential μ.

The initial state of the working body $E(0)$, $S(0)$, $N(0)$, and $V(0)$ is given. E and S are internal energy and entropy. The working body's variables are linked by the equation of state

$$E(0) = E(S(0), N(0), V(0))$$

The duration of the process τ and its entropy $S(\tau)$ are given. The combined volume of the source and working body is constant.

The maximal work problem (maximization of the energy extracted from the system) is equivalent to minimization of the internal energy at $t = \tau$

$$A = [E(0) - E(\tau) + E^0(0) - E^0(\tau)] \to \max \tag{3}$$

Since the increments of working body's entropy and temperature are given, $\Delta E = T\Delta S$ is fixed and the problem is reduced to maximization

$$\Delta E^0 = E^0(0) - E^0(\tau) = \int_0^\tau \mu^0 g(\mu^0,\mu)\,\mathrm{d}t \to \max_{\mu(t)} \tag{4}$$

subject to

$$\int_0^\tau \mu(t) g(\mu^0,\mu)\,\mathrm{d}t = T\Delta S \tag{5}$$

This is an averaged nonlinear programming problem.[23] Its optimal solution $\mu^*(t)$ is either a time-independent or a piecewise constant function of time that takes not more values than the number of constraints (eq 5) plus one. These values this function takes are called *basic* values. In our case there is no more than two basic values. They are determined from the following condition on the Lagrange function of the problem (eqs 4 and 5)

$$L = \left\{ g(\mu^0,\mu)(\mu^0 - \lambda\mu) + \lambda\frac{T\Delta S}{\tau} \right\} \to \min_{\mu} \max_{\lambda} \tag{6}$$

After one or two basic values of μ^* are found using (6), we then calculate $N^*(t)$ using the following equation:

$$\frac{\mathrm{d}N}{\mathrm{d}t} = g(\mu^0,\mu), \quad N(0) \text{ is fixed}$$

$N^*(t)$ is either a linear or a piecewise linear function. In the former case its slope is $g(\mu^0,\mu^*)$ and in the latter the slope is $g(\mu^0,\mu_1^*)$ on the interval $0,\gamma\tau$ and is $g(\mu^0,\mu_2^*)$ outside of this interval. γ is to be found from the condition

$$\gamma\mu_1^* g(\mu^0,\mu_1^*) + (1-\gamma)\mu_2^* g(\mu^0,\mu_2^*) = T\Delta S/\tau$$

If the Lagrange function L is convex on μ, that is, if

$$\frac{\mathrm{d}^2 g}{\mathrm{d}\mu^2} > 2\lambda\frac{\mathrm{d}g}{\mathrm{d}\mu}$$

then only the one basic value exists.

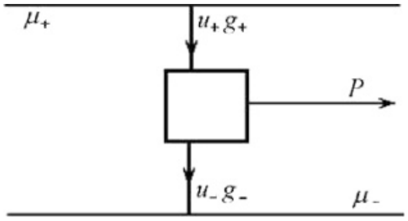

Figure 1. Structure of a diffusion engine with continuous contact between the working body and the reservoirs.

One can show that solution has physical meaning if and only if $\lambda > 0$ and $\mathrm{d}g/\mathrm{d}\mu < 0$. Therefore, for the majority of real dependencies $g(\mu)$ the condition that L is convex holds, μ^* is constant and is determined by the equation

$$\mu g(\mu^0,\mu) = \frac{T\Delta S}{\tau}$$

$$N^*(\tau) = N_0 + g(\mu^0,\mu^*)\tau$$

$$\Delta E^\circ = \mu^0 g(\mu^0,\mu^*)\tau \tag{7}$$

Its substitution into (3) yields A^*. For a separation problem, this value corresponds to the minimum of work and is always negative.

Suppose $g(\mu^0,\mu) = \alpha(\mu^0)(\mu^0 - \mu)$. The Lagrange function then takes the form

$$L = \alpha(\mu^0)(\mu^0 - \mu)(\mu^0 - \lambda\mu) + \lambda\frac{T\Delta S}{\tau}$$

It is convex on μ and has a single minimum at $\mu^* = \mu^0/2\lambda$. From (7), we get

$$\alpha(\mu^0)(\mu^0 - \mu^*)\mu^* = \frac{T\Delta S}{\tau}$$

and

$$\mu^* = \mu^0/2 + \sqrt{\mu^{02}/4 - \frac{T\Delta S}{\tau\alpha(\mu^0)}},$$

$$g^* = \alpha(\mu^0)\left(\mu^0/2 - \sqrt{\mu^{02}/4 - \frac{T\Delta S}{\tau\alpha(\mu^0)}}\right)$$

The optimal rate of change of the composition of the working body is constant and equal to g^*.

Maximal Power of Diffusion-Mechanical Cycle. Consider a system that includes working body and two reservoirs with different chemical potentials μ_+, and μ_- (for definiteness, $\mu_+ > \mu_-$) (Figure 1). The system's objective is to extract the maximal amount of work. The system operates cyclically and the increments of entropy, internal energy, and mass of the working body over the cycle are all equal to 0, over the cycle. The temperatures of all subsystems are the same.

Contact with Reservoirs in Turn. First, we consider the case when the working contacts each of two reservoirs in turn. τ denotes the cycle's period and $\mu_0(t)$ − reservoir's chemical potential, which takes two values, μ_+ and μ_-. Then the problem of obtaining the maximal work A in the given period τ takes the form

$$A = E_0(0) - E_0(\tau) = \int_\tau^0 \mu g(\mu_0,\mu)\,\mathrm{d}t \to \max_{\mu_0,\mu} \tag{8}$$

subject to constraints the cyclic condition

$$\Delta N = \int_\tau^0 g(\mu_0,\mu)\,\mathrm{d}t = 0 \tag{9}$$

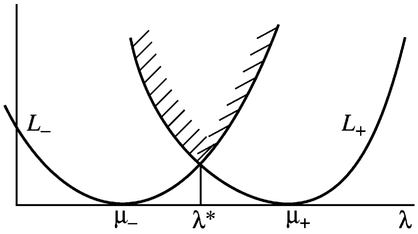

Figure 2. Characteristic dependence on λ of the maximum with respect to μ of the Lagrange function for $\mu_0 = \mu_+$ and $\mu_0 = \mu_-$.

This is again an average nonlinear programming problem whose solution is determined by the basic values of μ and μ_0. They are determined by the conditions of maximum of the Lagrange function of the problem (eqs 8 and 9) on μ_0 and μ and its minimum on λ

$$L = \{g(\mu_0,\mu)(\mu - \lambda)\} \rightarrow \max_{\mu_0,\mu} \min_{\lambda}$$

There are two basic values of μ_0. One corresponds to $\mu_0 = \mu_+$ and the other to $\mu_0 = \mu_-$. If the Lagrange function is strictly convex on μ, then the basic values obey the conditions

$$\frac{\partial L}{\partial \mu} = \frac{\partial g}{\partial \mu}(\mu - \lambda) + g(\mu_0,\mu) = 0$$

or

$$\frac{g(\mu_0,\mu)}{\mu \text{ - } \lambda} = -\frac{\partial g(\mu_0,\mu)}{\partial \mu}$$

We denote the root of this equation for $\mu_0 = \mu_-$ as μ_1 and for $\mu_0 = \mu_+$ as μ_2. Since L is maximal at the basic values

$$L(\mu_+,\mu_1,\lambda) = L(\mu_-,\mu_2,\lambda) \tag{10}$$

which determines λ.

Let us specify the obtained dependencies for

$$g(\mu_0,\mu) = \alpha(\mu_0)(\mu_0 - \mu)$$

From (10) we get

$$\mu_1 = \frac{\mu_+ + \lambda}{2}, \quad \mu_2 = \frac{\mu_- + \lambda}{2} \tag{11}$$

Substitution of μ_1 and μ_2 into L for each basic value gives the L dependence on λ

$$L_+ = L(\mu_+,\mu_1) = \frac{\alpha_+}{4}(\mu_+ - \lambda)^2$$

$$L_- = L(\mu_-,\mu_2) = \frac{\alpha_-}{4}(\mu_- - \lambda)^2$$

The minimum on λ of the maximum of L on μ_0, μ is attained here at λ^* (Figure 2)

$$L_+(\lambda) = L_-(\lambda) \Rightarrow \lambda^* = \frac{\sqrt{\alpha_+}\mu_+ + \sqrt{\alpha_-}\mu_-}{\sqrt{\alpha_+} + \sqrt{\alpha_-}} \tag{12}$$

The fractions of the cycle when there are contact with corresponding reservoir are determined by the condition (eq 9)

$$\gamma_+ = \frac{\alpha_-\sqrt{\alpha_+}}{\alpha_-\sqrt{\alpha_+} + \alpha_+\sqrt{\alpha_-}}$$

$$\gamma_- = \frac{\alpha_+\sqrt{\alpha_-}}{\alpha_-\sqrt{\alpha_+} + \alpha_+\sqrt{\alpha_-}}$$

The maximal work is

$$A^*(\tau) = \tau[\gamma_+\mu_1\alpha_+(\mu_+ - \mu_1) + \gamma_-\mu_2\alpha_-(\mu_2 - \mu_-)]$$

where μ_1 and μ_2 are to be found from (11) after λ from (12) is substituted into it. The maximal power is

$$\frac{A^*(\tau)}{\tau} = [\gamma_+\mu_1\alpha_+(\mu_+ - \mu_1) + \gamma_-\mu_2\alpha_-(\mu_2 - \mu_-)]$$

Continuous Contact with Reservoirs. It is possible that there is a uninterrupted, continuous contact between the working body of a heat engine and its reservoirs (a turbine). In this case, the parameters of the working body are distributed, and if they are driven by convective flux then they can be approximately described as reversible. Similarly in a system that is not homogeneous with respect to concentration (eg separation system or diffusion engine) it is possible to have a separation system/diffusion engine with continuous contact between the working body and reservoirs.

The maximal power problem then is reduced to a nonlinear programming problem

$$p = [g_1(\mu_+,\mu_1)\mu_1 - g_2(\mu_2,\mu_-)\mu_2] \rightarrow \max_{\mu_1\mu_2}$$

subject to

$$g_1(\mu_+,\mu_1) - g_2(\mu_2,\mu_-) = 0 \tag{13}$$

Its condition of optimality yields

$$\mu_1 - \mu_2 = \frac{g_2(\mu_2,\mu_-)}{\partial g_2/\partial \mu_2} - \frac{g_1(\mu_+,\mu_1)}{\partial g_1/\partial \mu_1} \tag{14}$$

which, jointly with (13), determines the problem's unknowns.

Suppose g_1 and g_2 are proportional to the difference of the chemical potentials

$$g_1 = \alpha_1(\mu_+ - \mu_1), \quad g_2 = \alpha_2(\mu_2 - \mu_-)$$

Then eq 14 takes the form

$$\mu_1 - \mu_2 = (\mu_2 - \mu_-) + (\mu_+ - \mu_1)$$

or

$$\mu_1 - \mu_2 = \frac{\mu_+ - \mu_-}{2} \tag{15}$$

From the condition $g_1 = g_2$, we get

$$\alpha_1\mu_1 + \alpha_2\mu_2 = \alpha_1\mu_+ + \alpha_2\mu_- \tag{16}$$

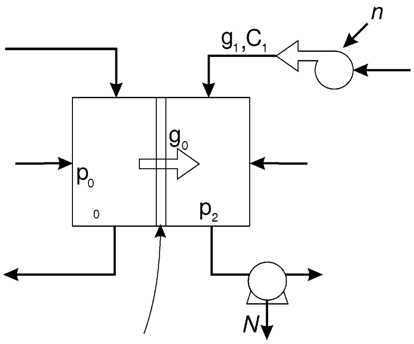

Figure 3. Structure of saline diffusion engine with constant contact between the working body and reservoirs.

The solution of (15) and (16) is

$$\mu_2^* = \frac{1}{2(\alpha_1 + \alpha_2)}[\mu_+\alpha_1 + \mu_-(\alpha_1 + 2\alpha_2)]$$

$$\mu_1^* = \frac{1}{2(\alpha_1 + \alpha_2)}[\mu_+(\alpha_2 + 2\alpha_1) + \mu_-\alpha_2]$$

The maximal power which corresponds to this solution is

$$p_{\max} = \frac{\bar{\alpha}}{4}(\mu_+ - \mu_-)^2$$

where the equivalent mass transfer coefficient is

$$\bar{\alpha} = \frac{\alpha_1\alpha_2}{\alpha_1 + \alpha_2}$$

3. Limiting Performance for Membrane Separation of Liquid Mixtures

Consider a system that consists of two liquids with the same temperatures separated by a semipermeable membrane. One of the liquids is a pure solvent and the second is a solvent mixed with a second liquid with the molar concentration C. The membrane is permeable only for the solvent. The system is in equilibrium when the chemical potentials calculated using (2) are the same, that is, when

$$v_0P_0 - v_rP_r = -RT\ln x_0$$

The subscript 0 here corresponds to the pure solvent and subscript r to the dilute solution, x_0 is the molar fraction of the solvent in the mixture and x_1 is the molar fraction of the substance that is dissolved in the solvent. The pressure difference on two sides on the membrane is denoted as π. We assume that molar concentrations are small and molar volumes υ_0 and υ_r are equal. We assume that x_1 is small and $\ln(x_0) = \ln(1 - x_1) \approx -x_1$. Then

$$\pi = RT\frac{x_1}{\upsilon_0} = RTC \tag{17}$$

where C is the concentration of the dissolved substance, π is the osmotic pressure, T is the temperature, and R is the universal gas constant.

Equation 17 is called the van't Hoff equation for osmotic pressure.

Consider the system shown in Figure 3.

The pure solvent is in the left chamber. The pressure there is the same external pressure p_0. The mixture is in the right chamber. Its volume is denoted as V and the concentration of the dissolved substance in it as C. The pressure in this chamber is p_2. We assume that the solution is ideal. In equilibrium, when the flow through the right chamber is equal zero, the pressure which sets in this chamber exceeds p_0 by the osmotic pressure π. This osmotic pressure is linked to the concentrations in this chamber and temperature via van't Hoff equation. If the mixture in the right chamber is replenished, then the pressure $p_2 < p_0 + \pi$. This drives the flow of solvent g_0 through the membrane. The usual assumption is that this diffusive flow is proportional to the difference between the actual and equilibrium pressures

$$g_0 = \alpha(p_0 + \pi - p_2) = \alpha(\pi - \Delta p) \tag{18}$$

where $\Delta p = p_2 - p_0$.

We denote the power of the pump that supplies feed mixture as n, its rate as g_1 and the concentration of the dissolved substance in the feed as C_1. Assuming that the pump has 100% efficiency, we get

$$n = \Delta p g_1$$

The flow through the membrane increases the volume in the right chamber, which drives the turbine and generates power N

$$N = (g_1 + g_0)\Delta p$$

The power and efficiency of the saline diffusion engine are

$$N_0 = N - n = g_0\Delta p = \alpha(\pi - \Delta p)\Delta p$$

$$\eta = \frac{N_0}{g_1} = \frac{\alpha(\pi - \Delta p)\Delta p}{g_1}$$

The efficiency is defined as work per concentrated solution's unit volume. We assume π is independent of Δp. In this case the power is maximal and equal to

$$\overline{N_0} = \alpha\frac{\pi^2}{4} = \frac{\alpha}{4}(CRT)^2$$

at $\Delta p = \pi/2$. Since $C < C_1$, this power is always lower than

$$\overline{N^*}_0 = \frac{\alpha}{4}(C_1RT)^2 \tag{19}$$

which gives an upper bound on the maximal power.

The bound (19) can be made more accurate if we take into account that g_0, Δp and C obey (18) as well as the mass balance with respect to the dissolved component

$$(g_1 + g_0)C = g_1C_1 \tag{20}$$

After expressing C and Δp in terms of g_0 (from (18), and (20)) and their substitution into N_0 and η, we get

$$C = \frac{g_1C_1}{g_1 + g_0}, \quad \Delta p = CRT - \frac{g_0}{\alpha} \tag{21}$$

$$N_0 = g_0\Delta p = \frac{RTC_1g_1g_0}{g_1 + g_0} - \frac{g_0^2}{\alpha} \tag{22}$$

$$\eta = \frac{\alpha(\pi - \Delta p)\Delta p}{g_1} = \frac{RTC_1g_0}{g_1 + g_0} - \frac{g_0^2}{\alpha g_1} \tag{23}$$

Both functions of g_0 in (22) and (23) are concave and have maxima at the same point g_0^*, which can be found from the maximum condition for any of them. We use the maximum of N_0 to find this optimal g_0^*. We get

$$\varphi(g_0) = g_0(g_1 + g_0)^2 = \frac{\alpha RT_{\mathrm{g}}{}^{2}{}_{1}C_1}{2} \tag{24}$$

It can be rewritten as

$$\frac{g^3{}_0}{g^2{}_1} + 2\frac{g^2{}_0}{g_1} + g_0 = \frac{\alpha RTC_1}{2} \tag{25}$$

we denote the expression in its right-hand side as M and its root as g_0^*. It is clear that it obeys

$$0 < g_0^* < M$$

The first approximation for g_0^* can be calculated using the chord method:[24]

$$\tilde{g}_0 = \frac{M}{M^2/g^2{}_1 + 2M^1/g_1 + 1} \tag{26}$$

Since the expression in the left-hand side of (25) is convex, $\tilde{g}_0 < g_0^*$.

If the difference between M and $\tilde{g}_0$ is not small enough, then this solution can be made more accurate suing tangent formula

$$g^1{}_0 = \tilde{g}_0 + \left(M - \frac{\tilde{g}^3{}_0}{g^2{}_1} - 2\frac{\tilde{g}^2{}_0}{g_1} - \tilde{g}_0\right)\left(\frac{3\tilde{g}^2{}_0}{g^2{}_1} + \frac{4\tilde{g}_0}{g_1} + 1\right) \tag{27}$$

The correction term is always positive and $g_0^1 > g_0^*$. The accuracy of this solution can be checked by substituting it into (24).

It is worth noting that the assumption about ideal solution leads to the constraint on the concentration of the working solution

$$C = C_1\frac{g_1}{g_1 + g_0}$$

This concentration cannot be too high otherwise the molecules of the dissolved substance will interact with each other and (17) will not hold.

Example. Let us find the maximal power N_0 and maximal efficiency η of diffusion engine with the following parameters: $g_1 = 0.000008$ m/s, $T = 298$ K, $R = 8.31$ J/(molK), and concentration of the dissolved substance (salt) in the input solution $\tilde{C}_1 = 40$ kg/m^3. Solt's molecular weight is $\mu = 0.05843$ kg/mol, and its molar concentration is $C_1 = 684.57$ mol/m^3. The membrane which separates compartments with concentrated and weak solutions is a standard industrial low adsorption acetate membrane filter with the pore size 0.2 μm, the average water flow rate is 4×10^{-7} m/s, and the pressure difference is 10^5 Pa. The membrane's mass transfer coefficient can be found using the water rate's dependence on pressure

$$g = \alpha\cdot\Delta p$$

From this equation, it follows that

$$\alpha = \frac{g}{\Delta p} = 4\cdot 10^{-8}\mathrm{m/(s\cdot N)}$$

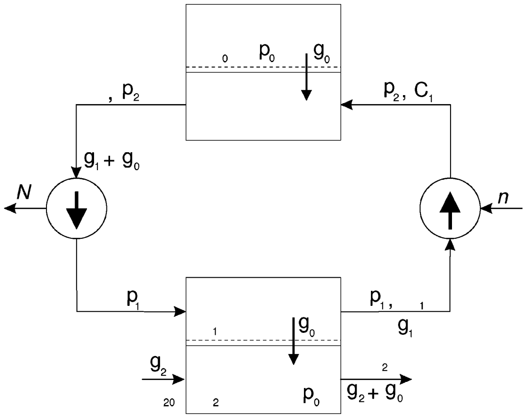

Figure 4. Structure of saline diffusion engine where the working body contacts reservoirs in turn.

The estimate (upper bound) on the diffusion engine's power given by (19) is

$$\overline{N^*{}_0} = 0.000287 \times 10^4\ \mathrm{W/(s\cdot m^2)}$$

Since $C < C_1$, this estimate is not accurate and should be corrected using formulas 24−27. We get $M = 3.39 \times 10^{-4}$. Then the first approximation given by (26) is

$$\tilde{g}_0 = 1.67 \times 10^{-6}\mathrm{m/s}$$

Since the distance between M and $\tilde{g}_0$ is large, one needs to calculate the second approximation g_0^1 using (27)

$$g^1{}_0 = 3.53 \times 10^{-6}\mathrm{m/s}$$

This g_0^1 is sufficiently close to g_0^* which maximizes the power and efficiency of the diffusion engine.

From (22) and (23), we find

$$N^*{}_0 = 1.03\ \mathrm{J/(s\cdot m^2)}$$

$$\eta^* = 0.129 \times 10^6\ \mathrm{J/m^5}$$

4. Saline Diffusion Engine Where the Working Body Contacts Reservoirs in Turn

The diffusion engine considered in the previous section operated stationary and uses the working body, which always stays in contact with both sources. One source supplied concentrated solution and the other supplied pure solvent. An alternative structure for a diffusive engine is shown in Figure 4. Here the working body contacts two reservoirs in turn, receiving solvent through one membrane and rejecting it into the concentrated solution through the other membrane. The pressure and the rate of the working body here change periodically. Pressure increases when the rate is lower (power n is spent) and decreases when the rate is higher (power N is generated).

We assume that no energy is drive the flow through the lower chamber, the concentration of the dissolved substance in the g_2 flow is equal 1 and the external pressure is p_0.

The power of this engine is

$$N_0 = N - n = (g_1 + g_0)\Delta p_{21} - g_1\Delta p_{21} = g_0\Delta p_{21}$$

where

$$\Delta p_{21} = p_2 - p_1$$

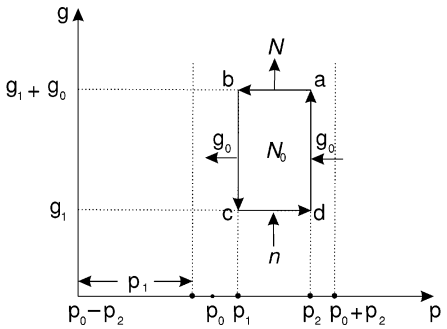

Figure 5. Cycle of the diffusion engine's working body.

We define the efficiency as the ration of N_0 to the rate of g_2

$$\eta = \frac{N_0}{g_2} = \frac{g_0}{g_2}\Delta p_{21}$$

The mass transfer kinetics is determined by the equations

$$g_0 = \alpha_1(p_0 + \pi - p_2) = \alpha_1(\pi - \Delta p_{20}) = \alpha_2[(p_1 + \pi_2) - (p_0 + \pi_1)] = \alpha_2(\Delta\pi_{21} + \Delta p_{10}) \quad (28)$$

Here $\Delta p_{20} = p_2 - p_0$, $\Delta\pi_{21} = \pi_2 - \pi_1$, and $\Delta p_{10} = p_1 - p_0$. Equation 28 gives cyclic condition for the working body's mass corresponds to the condition that the mass of the working body's mass.

Figure 5 shows the cycle of the working body of this diffusion engine.

The power n is equal to the area of the rectangular p_2dCp_1, and the power N to the area of p_2abp_1. The engine's power N_0 is equal to the area of the rectangular *abcd*.

First we assume that the osmotic pressures in the chambers and rates are independent. Then the maximal power problem for a diffusion engine takes the form

$$N_0 = (p_2 - p_1)g_0 \rightarrow \max_{p_1,p_2}$$

subject to

$$\alpha_1(p_0 + \pi - p_2) = \alpha_2(p_1 - p_0 + \pi_2 - \pi_1) = g_0 \quad (29)$$

From (29), we get

$$p_1 = \frac{g_0}{\alpha_2} + p_0 + \pi_1 - \pi_2$$

$$p_2 = p_0 + \pi - \frac{g_0}{\alpha_1}$$

We define the equivalent transfer coefficient

$$\bar{\alpha} = \frac{\alpha_1\alpha_2}{\alpha_1 + \alpha_2}$$

and get

$$p_2 - p_1 = \pi - \pi_1 + \pi_2 - \frac{g_0}{\bar{\alpha}}$$

Then

$$N_0 = g_0\left(\pi - \pi_1 + \pi_2 - \frac{g_0}{\bar{\alpha}}\right) = g_0\left(\pi + \Delta\pi_{21} - \frac{g_0}{\alpha}\right) \rightarrow \max_{g_0} \quad (30)$$

The maximum of this expression is

$$N^*{}_0 = \frac{\bar{\alpha}(\pi - \pi_1 + \pi_2)^2}{4} = \frac{\alpha(\pi + \Delta\pi_{21})^2}{4}$$

is achieved at

$$g^*{}_0 = \frac{\bar{\alpha}(\pi - \pi_1 + \pi_2)}{2} = \frac{\bar{\alpha}(\pi + \Delta\pi_{21})}{2}$$

Now we take into account the dependence of the osmotic pressures in chambers on concentration given by van't Hoff eq 17, Since these concentrations depend on rates g_1, g_2, and g_0, we get

$$\pi = CRT = C_1\frac{g_1RT}{g_1 + g_0}$$

$$\Delta\pi_{21} = (C_2 - C_1)RT = \left(\frac{g_2C_{20} + g_0C_1}{g_2 + g_0} - C_1\right)RT$$

Then expression 30 takes the form

$$\begin{aligned} N_0 &= g_0\left[RT\left(\frac{C_1g_1}{g_1 + g_0} + \frac{g_2C_{20} + g_0C_1}{g_2 + g_0} - C_1\right) - \frac{g_0}{\bar{\alpha}}\right] \\ &= g_0\left[RT\left(\frac{g_2C_{20} + g_0C_1}{g_2 + g_0} - \frac{C_1g_0}{g_1 + g_0}\right) - \frac{g_0}{\bar{\alpha}}\right] \rightarrow \max_{g_0} \end{aligned} \quad (31)$$

For the efficiency

$$\eta = \frac{g_0}{g_2}\left[RT\left(\frac{g_2C_{20} + g_0C_1}{g_2 + g_0} - \frac{C_1g_0}{g_1 + g_0}\right) - \frac{g_0}{\bar{\alpha}}\right] \rightarrow \max_{g_0} \quad (32)$$

Both criteria, (31) and (32), have the maximum on g_0 at the same point. Thus, we can use any one of them in the conditions of optimality to find g_0^*. The stationary nature of N_0 on g_0 yields the optimal flow

$$g_0 = \frac{\bar{\alpha}RT}{2}\left[\left(\frac{g^2{}_2C_{20} + 2g_0g_2C_1 + g^2{}_0C_1}{(g_2 + g_0)^2}\right) - C_1\frac{g_0(g_0 + 2g_1)}{(g_1 + g_0)^2}\right] \quad (33)$$

Substitution of (33) and solution $g_0^*(g_1, g_2, C_1)$ into N_0 and η yields the maximal power $N_0^*(g_1, g_2, C_1)$ and maximal efficiency $\eta^*(g_1, g_2, C_1)$. Since N_0^* and η^* are nonnegative, these equations single out thermodynamically feasible ranges for g_1, g_2, and C_1.

Example. Consider a diffusion engine where the working body contacts reservoirs in turn, $g_1 = 0.1$ m/s, $T = 298\ K$, $R = 8.31$ J/(mol·K), the concentration of the dissolved substance (salt) in the working body when it contacts concentrated solution is $\tilde{C}_1 = 30$ kg/m^3, and the salt's concentration in the input flow g_2 is $\tilde{C}_{20} = 50$ kg/m^3. Since the salt's molar weight is $\mu = 0.05843$ kg/mol, the molar concentrations are $C_1 = 513.43$ mol/m^3 and $C_{20} = 855.72$ mol/m^3. Since the amount of salt in the working body does not change over the cycle, $g_2 = g_1 = 0.1$ m/s. The same membrane is used as was used in the first example with mass transfer coefficients $\alpha = \alpha_+ = \alpha_- = 4 \times 10^{-8}$ m/(s·J) for contacts with both reservoirs.

Here $\bar{\alpha}$ is

$$\bar{\alpha} = \frac{4 \times 10^{-11} \times 4 \times 10^{-11}}{4 \times 10^{-11} + 4 \times 10^{-11}} = 2 \times 10^{-8} \mathrm{m/(s \cdot J)}$$

Let us find the optimal flow g_0^* which maximizes the power N^0 and the efficiency η. Here, (33) yields an equation for iterations

$$g_0^{i+1} = \frac{2 \times 10^{-11} \times 8.31 \times 10^7 \times 298}{2} \times \left[\left(\frac{10^2 \times 0.855 \times 10^{-3} + 2g_0^i 0.855 \times 10^{-3} \times 0.513 \times 10^{-3} + (g_0^i)^2 \times 0.513 \times 10^{-3}}{(10 + g^i{}_0)^2}\right) - \frac{0.513 \times 10^{-3} g_0^i (g_0^i + 2 \times 10)}{(10 + g_0^i)^2}\right] \tag{34}$$

We set $g_0^1 = 0.05$ m/s as the initial approximation of g_0^*. Iterating (34) gives $g_0^2 = 9.41 \times 10^{-7}$, $g_0^3 = 2.12 \times 10^{-6}$, and $g_0^4 = 2.12 \times 10^{-6}$. The third iteration gives a sufficiently accurate solution, so $g_0^* = 2.12 \times 10^{-6}$ m/s.

From (31) and (32), we now find the maximal N_0^* and η^*

$$N^*{}_0 = 2.2 \cdot \mathrm{J/(s \cdot m^2)}$$

$$\eta^* = 2.2 \times 10^5 \cdot \mathrm{J/m^5}$$

5. Conclusion

In this paper, the fundamental thermodynamic limits on the performance of a membrane separation system and a diffusion engine have been obtained.

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