steady-state reverse transport, according to our previous analysis.

In addition, the values obtained by means of Henderson's assumption agree with our exact computed results when r_θ is of the order of or greater than r, i.e., when the sufficient condition $r = r_\theta$ is fulfilled or the fixed charge concentration is high compared to bulk solution concentrations. (The computations carried out with smaller fixed charge concentrations showed that agreement between the exact results and those obtained by using Henderson's assumption was only possible for $r \approx r_\theta$.)

The exact membrane potential is nearly constant, irrespective of the fixed charge asymmetry. Henderson's assumption leads to values of membrane potential lower than the exact ones for $r_\theta < r$. The exact fluxes and those obtained via Henderson's assumption are also quite different. On the other hand, we see for the case $r = 10$ that the exact fluxes in the range $r_\theta \ll 1$ are almost twice those corresponding to a homogeneous membrane with $\theta(x) = \theta(d)$. This is not an asymmetry effect, since the mean fixed charge concentration in this range is approximately $\theta(d)/2$.

Discussion

We have considered a simple model for ion transport through inhomogeneous membranes whose asymmetric fixed charge distribution varies linearly with position inside the membrane. The numerical solution worked out here does not show the doubtful results arising from the use of the popular Henderson assumption in Takagi and Nakagaki's model and establishes some restrictive conditions for this assumption to be valid. However, the effects that the asymmetry exerts on the flux and the membrane potential have been found to be very small in our case, and more elaborate theories incorporating other asymmetry effects are now under development.

When we compare our results to experiment, a case of particular importance is that of $r = 1$. Experimental results[2,16] have shown nonzero values for the flux and membrane potential under this condition. According to our computations, these results should be regarded as of *transient* (not permanent) nature, as previously pointed out by Higuchi and Nakagawa.[5] This question deserves more attention. A necessary experimental condition for a nonzero asymmetric membrane potential when $r = 1$ is[16] "no permeation of ions across the membrane". (Under this condition the membrane potential is simply the sum of the two interfacial Donnan potentials, and this sum is not zero for $r = 1$ because of the fixed charge distribution asymmetry; see eqs 11 and 5.) This is an ideal limiting condition that can be approximated in practice with asymmetric membranes of high *compactness*. Just two examples: in ref 16, the membrane was so compact that "the membrane resistance was high and hardly depended on the salt concentration", and in ref 2, inspection of Figure 6B leads to the estimation $D_s \approx 10^{-9}$ cm^2/s for the membrane salt diffusion coefficient (this value is to be compared to the typical one, $D_s \approx 10^{-5}$ cm^2/s, for diffusion in a free electrolyte solution). Therefore, given an initial thermodynamic state of the membrane system, it would take a typical relaxation time $\tau_d = d^2/D_s \approx 10^5$ s (one day, approximately) for the diffusion through a membrane of thickness $d = 10^{-2}$ cm to reach the steady state (this state would be that of *equilibrium* for $r = 1$).

The above facts may suggest that the asymmetry effects observed for J and $\Delta\psi$ when $r = 1$ are not permanent, steady-state properties of the membrane system but depend on the initial thermodynamic state of this system. Thus, these effects will eventually vanish after some (long) relaxation time has passed, even if the external bulk solution concentration (the same at both sides of the membrane) is kept constant. (However, a complete theory for this transient behavior is clearly beyond the scope of the simple model considered here, and calls for a careful experimental analysis to guide it. Therefore, we prefer not to insist on these tentative comments at this stage.)

(16) Kamo, N.; Kobatake, Y. *J. Colloid Interface Sci.* **1974**, *46*, 85.

Estimation of Minimal Heat Consumption for Heat-Driven Separation Processes via Methods of Finite-Time Thermodynamics

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An analytical expression is obtained for a minimal average heat consumption of a separation process driven by heat from constant-temperature reservoirs. The classical equilibrium expression for heat consumption is obtained in the limit of an average feed flow of zero. A numerical method is proposed for computing the minimal heat consumption for reservoirs with variable temperatures. The analysis is based on energy, entropy, and material balances and on analogy with finite-time thermodynamics analysis of a heat engine with a nonuniform working fluid.

Introduction

Among all the categories of physical and chemical procedures, separation processes are probably the most wasteful of energy, when they are evaluated by free energy change from feed to products, per unit of energy used to drive the process, i.e., by the natural generalization of efficiency. The purpose of this paper is to lay the groundwork for analyzing the performance of separation processes and then to optimize that performance, especially when the process must operate at a nonzero rate.

Many heat-driven separation processes can be analyzed as heat engines, working between two reservoirs at different temperatures T_H and T_L and producing enthalpy and energy flows out of the system (instead of power output of conventional heat engines). In finite-time thermodynamics it is well-known that the average power output of a heat engine is bounded.[1,2] The analogue of this result for a separation process is the existence of an upper limit on the average enthalpy flow through the system when the average entropy flow through the system is fixed or a lower limit on the average entropy flow if the average enthalpy flow is fixed. With some additional assumptions on inputs and outputs this is equivalent to the existence of an upper limit for the average feed

(1) Curzon, F. L.; Ahlborn, B. *Am. J. Phys.* **1975**, *43*, 22.
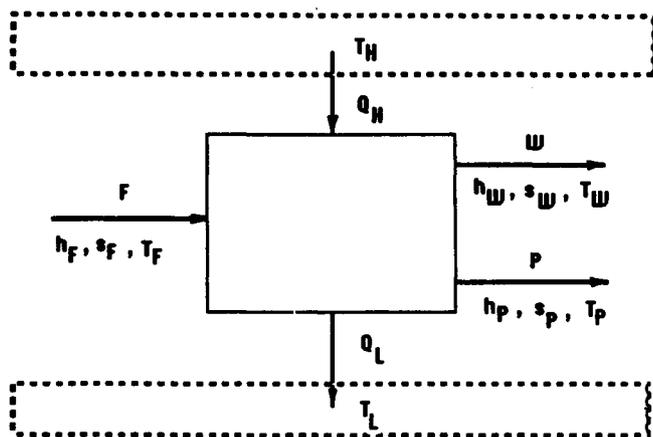(2) Orlov, V. N.; Berry, R. S. *Phys. Rev. A* **1990**, *42*, 7230.

Figure 1. Heat-driven separation process. F is the molar feed flow into the system per unit time, h_F and s_F are molar enthalpy and molar entropy of the feed, T_F is the temperature of the feed, P and W are molar product and waste flows out of system per unit time, and $T_H > T_L$ are the temperatures of the heat reservoirs.

flow into the system. It is also well-known that the efficiency of a heat engine at a maximum power point is lower than or equal to $1 - (T_L/T_H)^{1/2}$, where $T_H > T_L$ are the reservoir temperatures. This efficiency is less than the classical, reversible $1 - T_L/T_H$ because of the finite rate of the process with fixed nonzero average power. The same result is true for separation: the process with fixed nonzero average feed flow has a finite rate and its heat consumption is higher than the classical reversible heat consumption. We present here the analytical expression for minimum average heat consumption with fixed average enthalpy and entropy flows out of the system. As a corollary we get the same estimation for a binary separation process with fixed average feed flow into the system. Reversible heat consumption per mole of feed is obtained in the limit of zero average feed flow. Analytical expressions are obtained for the case of constant temperatures of the reservoirs. For time- and space-varying temperatures of the reservoirs we transform the problem of computing the minimal heat consumption to convex optimization and use numerical methods. The analysis is based on energy, material, and entropy balances and on a method[2] for solving averaged optimal control problems with the help of Lagrange multipliers.

Two previous articles[3,4] analyze separation processes using other methods and ideas of finite-time thermodynamics.

Energy requirements of separation processes are usually studied under the assumption of stationarity.[5-7] Here we analyze a more general class of weakly periodic processes, in which one can vary the feed flow and temperature in time and, in time and space, the reservoir temperatures. For heat engines such analysis was first carried out in ref 2.

Balances of Energy and Entropy for Separation

In this paper we analyze separation processes driven by heat. Such a process is shown schematically in Figure 1.

Under the assumptions of negligible potential and kinetic energy of flows F, P, and W (feed, product, and waste, respectively) and of Newtonian heat transfer on the boundary, the energy balance for the system has the form

$$dE/dt = Fh_F - Ph_P - Wh_W + \int_{A_H(t)} \alpha_H(T_H - T)\, da - \int_{A_L(t)} \alpha_L(T - T_L)\, da \quad (1)$$

(3) Mullins, O.; Berry, R. S. *J. Phys. Chem.* **1984**, *88*, 723.

(4) Brown, G. R.; Snow, S.; Andresen, B.; Salamon, P. *Phys. Rev. A* **1986**, *34*, 4370.

(5) King, C. J. *Separation Processes*; McGraw-Hill: New York, 1971.

(6) Henley, E. J.; Seader, J. D. *Equilibrium-Stage Separation Operations in Chemical Engineering*; Wiley: New York, 1981.

(7) Pratt, H. R. C. *Countercurrent Separation Processes*; Elsevier Publishing Co.: New York, 1967.

where $E(t)$ is a total energy of the system; F, P, and W are molar flows of feed, product, and waste material; h_F, h_P, and h_W are molar enthalpies of the flows; $\alpha_H = \alpha_H(\xi)$ is a heat-transfer coefficient between the high-temperature reservoir and the system; $\alpha_L = \alpha_L(\xi)$ is a heat transfer coefficient between the low-temperature reservoir and the system; $T_H(t,\xi)$ and $T_L(t,\xi)$ are the temperatures of the high- and low-temperature reservoirs, correspondingly; $T(t,\xi)$ is the temperature of the system; and $A_H(t)$ and $A_L(t)$ are the contact surfaces. Here $\xi = (\xi_1,\xi_2,\xi_3)$ is a vector of coordinates of a point in some Cartesian system; integration in (1) is carried out over the area of the surfaces A_H and A_L.

The entropy balance has the form

$$\frac{dS}{dt} = Fs_F - Ps_P - Ws_W + \int_{A_H(t)} \frac{\alpha_H(T_H - T)}{T}\, da + \int_{A_L(t)} \frac{\alpha_L(T_L - T)}{T}\, da + \sigma(t) \quad (2)$$

where $S(t)$ is the total entropy of the system, and $\sigma(t) \geq 0$ is the total entropy production inside the system.

We do not specify here whether the separation process is distillation, thermal diffusion, absorption, or something else. All we need in our analysis is the fact that for any specific separation process we have the inequality $\sigma(t) \geq 0$.

The weakly periodic process is defined as a process with $E(0) = E(\tau)$ and $S(0) = S(\tau)$, where time τ is the period of the process.

Let us now calculate the classical reversible minimal average amount of heat per cycle Q_H^{rev}, which is required for separation in a weakly periodic process. In this calculation temperatures T_H and T_L are considered to be constant. We let $\bar{f} = (1/\tau)\int_0^\tau f(t)\, dt$, $f_h(t) = Ph_P + Wh_W - Fh_F$, $f_s(t) = Ps_P + Ws_W - Fs_F$. From (1) for a weakly periodic process, it follows that

$$Q_H - Q_L = \bar{f}_h \quad (3)$$

where $Q_H = (1/\tau)\int_0^\tau \int_{A_H(t)} \alpha_H(T_H - T)\, da\, dt$ is the average heat flow into the system from the high-temperature reservoir and $Q_L = (1/\tau)\int_0^\tau \int_{A_L(t)} \alpha_L(T - T_L)\, da\, dt$ is the average heat flow out of the system into the low-temperature reservoir. From (2) we have

$$\frac{Q_H}{T_H} - \frac{Q_L}{T_L} = \bar{f}_s + \delta \quad (4)$$

where

$$\delta = -\frac{1}{\tau}\int_0^\tau \left\{ \sigma(t) + \int_{A_H(t)} \alpha_H(T_H - T)\left(\frac{1}{T} - \frac{1}{T_H}\right) da + \int_{A_L(t)} \alpha_L(T_L - T)\left(\frac{1}{T} - \frac{1}{T_L}\right) da \right\} dt$$

It is easy to see that $\delta \leq 0$, with the equality holding for reversible process. From (3) and (4) follows

$$Q_H = \frac{\bar{f}_h - T_L\bar{f}_s - T_L\delta}{1 - T_L/T_H} \quad (5)$$

From the equality 5 and the inequality $\delta \leq 0$ we obtain the inequality

$$Q_H \geq \frac{\bar{f}_h - T_L\bar{f}_s}{1 - T_L/T_H} = Q_H^{rev} \quad (6)$$

For a stationary process inequality (6) is equivalent to the inequality for net work $W_n \geq \Delta B_{sep}$ (see ref 5, p 634), where $\Delta B_{sep} = \Delta H - T_0\Delta S$ is the change in availability, and $W_n = Q_H(T_H - T_0)/T_H - Q_L(T_L - T_0)/T_L$. In our notations $\Delta H = f_h$ and $\Delta S = f_s$. An estimate similar to (6) was used in ref 8 in the analysis of the efficiency of rectification.

For typical, real separation processes the consumption of the heat is much higher than the right-hand side of inequality (6).

(8) Malykh, V. L. *Teor. Osn. Khim. Tekhnol.* **1989**, *23*, 723 (in Russian).

Having this in mind, we shall try to find a more realistic lower bound for the heat consumption by taking into account the finite time of the process, and the corresponding finite values of heat flows, finite thermal resistance, etc.

Minimal Average Heat Consumption Problem

For a heat-driven separation process the average heat consumption could be calculated via

$$Q_H = (1/\tau) \int_0^\tau \int_{A_H(t)} \alpha_H(T_H - T) \, da \, dt \qquad (7)$$

if we knew the temperature $T(t,\xi)$ of the system. But to find this temperature, we would have to specify our model more precisely. We shall not do this. Instead, we shall use only (1), (2), and the fact that in any process $T(t,\xi) > 0$. We shall consider the function $T(t,\xi)$ as a control and solve the following:

Problem 1: Given the functions $f_h(t)$ and $f_s(t)$, maximize $-Q_H$ with constraints $E(0) = E(\tau)$ and $S(0) = S(\tau)$.

Problem 1 is a typical averaged optimal control problem, similar to the problems solved in ref 2 for the heat engine. The only difference is the nonzero term $f_s(t)$ in (2). For our purposes it is enough to get an upper bound for the criteria of problem 1. We shall do this with the help of Lagrange multipliers. The problem has two constraints and with the help of Lagrange multipliers can be formally reduced to a two-dimensional convex optimization problem. But we shall reduce problem 1 to a one-dimensional convex optimization with the help of the solution of the following:

Problem 2: Given the function $f_s(t)$, maximize $Q_H - Q_L$ with the constraint $S(0) = S(\tau)$.

Problem 2 is also a typical averaged optimal control problem. It is similar to the problem of finding maximum average power output.[2] The only difference is again the nonzero term $f_s(t)$ in (2). Problem 2 has one constraint, so, with the help of a Lagrange multiplier, it can be transformed to a one-dimensional convex optimization.

Transformation to Convex Optimization Problems

Let us first consider problem 2. The upper bound for criteria in this problem can be obtained by solving an unconstrained averaged problem 2': maximize

$$L_2 = Q_H - Q_L + \frac{\lambda}{\tau} \int_0^\tau \left\{ \int_{A_H(t)} \frac{\alpha_H(T_H - T)}{T} \, da + \int_{A_L(t)} \frac{\alpha_L(T_L - T)}{T} \, da \right\} dt - \lambda \bar{f_s}$$

over the range of admissible control $T > 0$. Here $\lambda < 0$, and we omit the nonpositive term $\lambda \bar{\sigma}$. We denote $\phi_2(T_H,T_L,\bar{f_s},\lambda) = \max_{T>0} L_2$. It is easy to see that for $\lambda < 0$ maximization with $T > 0$ can be carried out analytically and we have the upper bound

$$\phi_2 = \frac{1}{\tau} \int_0^\tau \left\{ \int_{A_H} \alpha_H (T_H^{1/2} - (-\lambda)^{1/2})^2 \, da + \int_{A_L} \alpha_L (T_L^{1/2} - (-\lambda)^{1/2})^2 \, da \right\} dt - \lambda \bar{f_s} \quad (8)$$

The best (least) upper bound is $\mathcal{P}(T_H,T_L,\bar{f_s}) = \min_\lambda \phi_2(T_H,T_L,\bar{f_s},\lambda)$. Differentiating (8) with respect to λ, we find the expression for optimum $\hat{\lambda}$, which has the form

$$\sqrt{-\hat{\lambda}} = \overline{(a_H \alpha_H \sqrt{T_H})} + \overline{(a_L \alpha_L \sqrt{T_L})}/(\gamma_H + \gamma_L + \bar{f_s}) \quad (9)$$

where $a_H(t)$ is the area of the surface $A_H(t)$, $a_L(t)$ is the area of the surface $A_L(t)$, $g_H = (1/\tau) \int_0^\tau (1/a_H) \int_{A_H(t)} g_H(t,\xi) \, da \, dt$, $g_L = (1/\tau) \int_0^\tau (1/a_L) \int_{A_L(t)} g_L(t,\xi) \, da \, dt$, $\gamma_H = \overline{a_H \alpha_H}$, $\gamma_L = \overline{a_L \alpha_L}$. Functions g_H and g_L are used here only to define the averagings. Substituting (9) into (8), we get an analytical expression for the functional

$$\mathcal{P}(T_H,T_L,\bar{f_s}) = \phi_2(T_H,T_L,\bar{f_s},\hat{\lambda}(T_H,T_L,\bar{f_s})) \quad (10)$$

The first two arguments of this functional are the functions $T_H(t,\xi)$,

$T_L(t,\xi)$; the third argument is the scalar $\bar{f_s}$. This functional solves problem 2' and gives the estimate

$$\bar{f_h} \le \mathcal{P}(T_H,T_L,\bar{f_s}) \quad (11)$$

for average enthalpy flow, which follows from $Q_H - Q_L = \bar{f_h}$. In the next section, we shall use inequality (11) to get the value of the maximum average feed flow into the system.

Let us now consider problem 1. The upper bound for the criterion in this problem can be obtained by solving the unconstrained averaged problem 1': maximize

$$L_1 = -Q_H + l(Q_H - Q_L) + \frac{\lambda}{\tau} \int_0^\tau \left\{ \int_{A_H(t)} \frac{\alpha_H(T_H - T)}{T} \, da + \int_{A_L(t)} \frac{\alpha_L(T_L - T)}{T} \, da \right\} dt - \lambda \bar{f_s} - l\bar{f_h}$$

over the range of the admissible control $T > 0$. Here $\lambda < 0$, and we again omit the nonpositive term $\lambda \bar{\sigma}$. We denote $\phi_1(T_H,T_L,\bar{f_s},\bar{f_h},\lambda,l) = \max_{T>0} L_1$. For $\lambda < 0$ maximization in $T > 0$ can be carried out analytically, and we get

$$\phi_1 = \frac{1}{\tau} \int_0^\tau \left\{ \int_{A_H} \alpha_H ((T_H(l-1))^{1/2} - (-\lambda)^{1/2})^2 \, da + \int_{A_L} \alpha_L ((T_L l)^{1/2} - (-\lambda)^{1/2})^2 \, da \right\} dt - \lambda \bar{f_s} - l\bar{f_h}$$

The best (least) upper bound of ϕ_1 is obtained minimizing this convex function in the variables λ and l. Minimizing first in the variable λ, we get $\psi_1(T_H,T_L,\bar{f_s},\bar{f_h},l) = \min_\lambda \phi_1$. The functional ψ_1 is expressed with the help of the functional $\mathcal{P}(10)$ in the following way:

$$\psi_1 = \mathcal{P}((l-1)T_H,lT_L,\bar{f_s}) - l\bar{f_h} \quad (12)$$

Let $\psi_1(T_H,T_L,\bar{f_s},\bar{f_h},\hat{l}) \le \psi_1(T_H,T_L,\bar{f_s},\bar{f_h},l)$ for all $l > 1$. Then the best upper bound for problem 1 is $\psi_1(T_H,T_L,\bar{f_s},\bar{f_h},\hat{l})$. Corresponding minimal heat consumption in the separation process is $Q_H^{min}(T_H,T_L,\bar{f_s},\bar{f_h}) = -\psi_1(T_H,T_L,\bar{f_s},\bar{f_h},\hat{l})$, and the corresponding estimate is

$$Q_H \ge Q_H^{min} \quad (13)$$

It is easy to see that $Q_H^{min}(T_H,T_L,\bar{f_s},\bar{f_h})$ is convex in the variables $\bar{f_s}$ and $\bar{f_h}$ and $\partial Q_H^{min}/\partial \bar{f_s} = \hat{\lambda}$, $\partial Q_H^{min}/\partial \bar{f_h} = \hat{l}$. From these equalities and $\lambda < 0$, $l > 1$ follows that Q_H^{min} is strictly monotonically decreasing in the argument $\bar{f_s}$ and strictly monotonically increasing in the argument $\bar{f_h}$. It is also easy to see that the function $\psi_1(T_H,T_L,\bar{f_s},\bar{f_h},l)$ is convex in the variable l and that $d\psi_1/dl \to -\infty$ when $l \to 1$. The condition $\lim_{l\to+\infty} \psi_1/l > 0$ guarantees the existence of a minimum point. Using the fact that $\mathcal{P}(aT_H,aT_L,\bar{f_s}) = a\mathcal{P}(T_H,T_L,\bar{f_s})$ for $a > 0$, we get the equivalent condition $\mathcal{P}(T_H,T_L,\bar{f_s}) > \bar{f_h}$, which is just the strict form of inequality (11).

For heat-driven separation processes it is reasonable to assume that $\bar{f_h} \ge 0$. This implies, according to (11), $\mathcal{P}(T_H,T_L,\bar{f_s}) \ge 0$. The last inequality gives us the lower bound for $\bar{f_s}$. Indeed, let $\mathcal{P}(T_H,T_L,\bar{f_s}^{min}) = 0$. Then $\bar{f_s} \ge \bar{f_s}^{min}$ because $\mathcal{P}$ is strictly monotonically increasing in the argument $\bar{f_s}$.

Given functions $\alpha_H(\xi)$, $T_H(t,\xi)$ and $\alpha_L(\xi)$, $T_L(t,\xi)$ defined on the surfaces $A_H(t)$ and $A_L(t)$, correspondingly, and flows $f_s(t)$ and $f_h(t)$ of entropy and enthalpy, we are able to compute the minimal heat consumption by solving a one-dimensional convex minimization problem for the function ψ_1. For constant-temperature reservoirs, this minimization is carried out analytically in the next section.

Analytical Expressions for Minimal Heat Consumption

The function ψ_1, eq 12, can be presented in the form $\psi_1 = a_1(-(l(l-1))^{1/2} + a_2 l + a_3)$. For constant temperatures T_H and T_L, the coefficients a_1, a_2, and a_3 are the following:

$$a_1 = \frac{2\gamma_H\gamma_L(T_HT_L)^{1/2}}{\gamma_H + \gamma_L + \bar{f_s}}$$

$$a_2 = \frac{b_2 + c_2}{2\gamma_H\gamma_L(T_HT_L)^{1/2}(\gamma_H + \gamma_L + \bar{f_s})} - \frac{\bar{f_h}}{a_1}$$

$$a_3 = -\left(\frac{T_H}{T_L}\right)^{1/2}\frac{(\gamma_H + \bar{f_s})^2 + \gamma_L\gamma_H + \bar{f_s}\gamma_H}{2\gamma_L(\gamma_H + \gamma_L + \bar{f_s})}$$

where

$$b_2 =$$
$$\gamma_H(\gamma_L + \bar{f_s})^2T_H + \gamma_L{}^2\gamma_HT_L + \gamma_L(\gamma_H + \bar{f_s})^2T_L + \gamma_H{}^2\gamma_LT_H$$

$$c_2 = \bar{f_s}(\gamma_H{}^2T_H + \gamma_L{}^2T_L)$$

Condition $a_2 > 1$ is equivalent to the condition $\mathcal{P}(T_H,T_L;\bar{f_s}) > \bar{f_h}$. It is easy to see that the function ψ_1 has a minimum in the variable l at

$$\hat{l} = [1 + (1 + (a_2{}^2 - 1)^{-1})^{1/2}]/2$$

The minimal heat consumption is $Q_H^{min} = -\psi_1(T_H,T_L;\bar{f_s},\bar{f_h},\hat{l})$. Using the homogeneity of the function $\mathcal{P}$ in the first two arguments, we could obtain another expression for minimal heat consumption. Indeed, differentiating (12) in l, we have

$$\frac{\partial\mathcal{P}}{\partial T_H}((\hat{l}-1)T_H,\hat{l}T_L;\bar{f_s})T_H + \frac{\partial\mathcal{P}}{\partial T_L}((\hat{l}-1)T_H,\hat{l}T_L;\bar{f_s})T_L = \bar{f_h}$$

From homogeneity, it follows that

$$\frac{\partial\mathcal{P}}{\partial T_H}((\hat{l}-1)T_H,\hat{l}T_L;\bar{f_s})(\hat{l}-1)T_H +$$
$$\frac{\partial\mathcal{P}}{\partial T_L}((\hat{l}-1)T_H,\hat{l}T_L;\bar{f_s})\hat{l}T_L = \mathcal{P}$$

Substituting the first equality multiplied by $\hat{l}$ into the second, we get $(-\partial\mathcal{P}/\partial T_H)T_H + \hat{l}\bar{f_h} = \mathcal{P}$. From the last equality we obtain

$$Q_H^{min} = \frac{\partial\mathcal{P}}{\partial T_H}((\hat{l}-1)T_H,\hat{l}T_L;\bar{f_s})T_H \qquad (14)$$

Using (14), the expression

$$\mathcal{P} =$$
$$\{\gamma_H[(T_H)^{1/2}(\gamma_L + \bar{f_s}) - \gamma_L(T_L^{1/2})]^2 + \gamma_L[(T_L^{1/2})(\gamma_H + \bar{f_s}) - \gamma_H(T_H^{1/2})]^2 + \bar{f_s}(\gamma_H(T_H^{1/2}) + \gamma_LT_L^{1/2})^2\}/(\gamma_H + \gamma_L + \bar{f_s})^2 \qquad (15)$$

the equality $[\hat{l}/(\hat{l}-1)]^{1/2} = a_2 + (a_2{}^2 - 1)^{1/2}$, and the notation $\kappa = \gamma_L(T_L/T_H)^{1/2}(a_2 + (a_2{}^2 - 1)^{1/2})$, we get the minimal heat consumption in the form

$$Q_H^{min} = \frac{T_H\gamma_H(\gamma_L - \kappa + \bar{f_s})}{\gamma_H + \gamma_L + \bar{f_s}} \qquad (16)$$

As mentioned in the previous section, the function $Q_H^{min}(T_H,T_L;\bar{f_s},\bar{f_h})$ is strictly monotonically decreasing in the argument $\bar{f_s}$ and is strictly monotonically increasing in the argument $\bar{f_h}$. $\bar{f_h},\bar{f_s} \geq 0, \bar{f_s} \geq \bar{f_s}^{min}$. The value of $\bar{f_s}^{min}$ is calculated by using (15) via solving the quadratic equation $\mathcal{P} = 0$. The result is

$$\bar{f_s}^{min} = (-b + (b^2 - 4ac)^{1/2})/(2a) \qquad (17)$$

where

$$a = \gamma_HT_H + \gamma_LT_L$$

$$b = (\gamma_H(T_H)^{1/2} - \gamma_L(T_L)^{1/2})^2 + 2\gamma_H\gamma_L(T_H + T_L)$$

$$c = \gamma_H\gamma_L(\gamma_H + \gamma_L)[(T_H)^{1/2} - (T_L^{1/2})]^2$$

From (4) and (5) it follows that

$$Q_H^{min} \geq \frac{\bar{f_h} - T_L\bar{f_s}}{1 - T_L/T_H} \qquad (18)$$

Let us show now that Q_H^{min} tends to the reversible heat consumption when the average feed flow tends to zero. For this

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TABLE I: Ratio of the Rate-Constrained Minimum Heat Consumption Q_H^{min} to the Reversible Limit of Minimum Heat Consumption Q_H^{rev}, for Various Values of the Excess Entropy Flow Parameter C and the Excess Enthalpy Flow Parameter D (See Text)

C	D					
	1.0	0.8	0.6	0.4	0.2	0.0
0.8	1.98	1.66	1.55	1.47	1.43	1.39
0.6	1.96	1.54	1.42	1.37	1.28	1.23
0.4	1.93	1.45	1.32	1.24	1.18	1.13
0.2	1.90	1.39	1.25	1.17	1.16	1.07

purpose we must accept some new assumptions. The material balances for binary separation process have the form

$$dN/dt = F - P - W \qquad dN_x/dt = x_FF - x_PP - x_WW \qquad (19)$$

where $N(t)$ is the number of moles of material in the system, $N_x(t)$ is the number of moles of the more volatile component in the system, x_F is a mole fraction of the more volatile component of the feed flow, and x_P and x_W are mole fractions of the more volatile component in the product flow P and waste flow W correspondingly. We assume here that (1) the separation process under consideration is binary, (2) molar fractions x_F, x_P, and x_W, enthalpies h_F, h_P, and h_W, and entropies s_F, s_P, and s_W are stationary, that is, independent of time, and (3) the process is weakly periodic in material, that is, $N(0) = N(\tau)$. With these assumptions from (19) follows $\bar{P} = [(x_F - x_W)/(x_P - x_W)]F$, $\bar{W} = [(x_P - x_F)/(x_P - x_W)]F$, $\bar{f_h} = r_hF$, and $\bar{f_s} = r_sF$, where $r_h = h_P(x_F - x_W)/(x_P - x_W) + h_W(x_P - x_F)/(x_P - x_W) - h_F$, $r_s = s_P(x_F - x_W)/(x_P - x_W) + s_W(x_P - x_F)/(x_P - x_W) - s_F$.

Substituting these expressions into (18), we get

$$Q_H^{min}(T_H,T_L;r_sF,r_hF) \geq \frac{r_h - T_Lr_s}{1 - T_L/T_H}F \qquad (20)$$

Using the analytical expression (16) for Q_H^{min}, one can show that

$$\frac{Q_H^{min}(T_H,T_L;r_sF,r_hF)}{F} \rightarrow \frac{r_h - T_Lr_s}{1 - T_L/T_H}$$

when $F \rightarrow 0$. For $r_s < 0$ and $r_h > 0$ the function $q(F) = Q_H^{min}(T_H,T_L;r_sF,r_hF)$ is convex and strictly monotonically increasing, which means that the average heat consumption increases with the growth of the average feed flow. From inequality (11), it follows that we could not increase the average feed flow F to infinity. There is an upper limit for average feed flow F^{max}, which is the solution of the equation

$$Fr_h = \mathcal{P}(T_H,T_L;r_sF) \qquad (21)$$

Indeed, for $r_s < 0$ and $r_h > 0$ the function $p(F) = \mathcal{P}(T_H,T_L;r_sF)$ is concave, strictly monotonically decreasing, and $p(0) = (\gamma_H\gamma_L/(\gamma_H + \gamma_L))(T_H^{1/2} - T_L^{1/2})^2 > 0$. These properties guarantee the existence and the uniqueness of the solution of eq 21.

Evaluating $q(F)$ at F^{max} using (16) with $a_2 = 1$, we get

$$q(F^{max}) =$$
$$\frac{T_H\gamma_H\gamma_L}{\gamma_H + \gamma_L + r_sF^{max}}\left(1 - \left(\frac{T_L}{T_H}\right)^{1/2} + r_sF^{max}/\gamma_L\right) \qquad (22)$$

Expression (22) is the analogue of the corresponding expression $\eta = 1 - (T_L/T_H)^{1/2}$ for the efficiency evaluated at the maximum power point. It gives us the minimum heat consumption at the maximum flow point.

Illustrative Calculations and Discussion

We computed the ratio Q_H^{min}/Q_H^{rev} for the propylene–propane distillation column (ref 6, p 686). In this process $T_H = 377.6$ K (220 °F), $T_L = 294.3$ K (70 °F). The measured values of the heat transfer coefficients α_H and α_L and contact areas a_H and a_L for this process are not available, so we assumed physically reasonable values of $\gamma_H = \alpha_Ha_H = 13\,000$ kg K^{-1} s^{-1} M^2, and $\gamma_L = \gamma_H$. With these data we computed $\bar{f_s}^{min}$ using (17).

Table I shows the ratio Q_H^{min}/Q_H^{rev} for different dimensionless parameters C and D, connected with the entropy and enthalpy

flows $\bar{f}_s$ and $\bar{f}_h$ by the formulas $\bar{f}_s = C\bar{f}_s^{min}$ and $\bar{f}_h = D\mathcal{P}(T_H,T_L,\bar{f}_s)$. Calculations carried out for other reasonable temperatures T_H and T_L and constants γ_H and γ_L gave qualitatively the same results.

From Table I one can see that minimal heat consumption calculated using (16) may be up to about twice the reversible heat consumption (6). The finite-time thermodynamic estimate (16) may be useful to compare two or more different separation technologies: examining heat-driven separation processes with measured real heat consumption one gets an estimate, more realistic than a comparison with the reversible limit, of the extent to which it is possible to improve the process. For processes with time- and space-dependent parameters, one has to minimize (12) in order to find the minimum heat consumption.

A provocative conclusion can now be drawn from the quantitative results: the constraint of realistic, nonzero flow reduces the limits of efficiency of separations, but to values still far above typical performances of real separation processes. The inference is that separation science offers opportunity for innovation, because the possibility exists to find inventive ways to perform heat-driven separation processes far more efficient than those now in use.

Dielectric Relaxation in Supercooled Triphenylchloromethane and Intrinsic Factor Determining Mobility in Molecular Liquids

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The heat capacity of the liquid, the supercooled liquid, the crystal, and the glass and dielectric properties of the supercooled liquid has been obtained for triphenylchloromethane (TPCM). Variations of dielectric relaxation with temperature and pressure are analyzed with respect to activation variables and configurational quantities, and compared with earlier results on *o*-terphenyl (*o*-TP), the mixture of TPCM/*o*-TP, and poly(vinyl chloride) (PVC). $P_i V^*/E^*$ of both TPCM and *o*-TP, where P_i, V^*, and E^* are the internal pressure, the volume of activation, and the internal energy of activation, respectively, is smaller than 0.5. The configurational entropy and/or internal energy governs the molecular mobility in TPCM as well as in *o*-TP and PVC. The intermolecular inefficient spaces of futile interstices among molecules, but not the intramolecular conformational degrees of freedom, may be the essential origin of the failure of free volume theories for mobility in molecular liquids. The intrinsic factors determining mobility may be the configurational internal energy and the configurational entropy in a region of lower densities without strong intermolecular forces. For small sphere molecules or their mixtures, the free volume also may be a good approximation.

Introduction

It has been well verified that the configurational entropy rather than the free volume determines molecular mobility and the glass transition of polymers accompanying large intramolecular rotational (conformational) entropy.[1-7] The validity of entropy theories has been explained more or less by the conformational degrees of freedom such as the flexibility of chain molecules.[8] From a consideration with the hole model,[9] Nose suggested that the conformational contribution to the entropy and heat capacity of liquids would be the origin of the failure of free volume theories.[10-13] Then one may expect nonassociated molecules with only a few conformational degrees of freedom to follow the free volume theories. When free volume theories hold, the Prigogine–Defay ratio[14] is unity, and the glass transition is approximated by the quasi-equilibrium Ehrenfest type second-order transition.

In a series of inclusive tests on the factors determining molecular mobility and the glass transition, we have obtained two inconsistent results for nonassociated molecules with only a few conformational degrees of freedom. The result for a mixture of triphenylchloromethane (TPCM) and *o*-terphenyl (*o*-TP) in a weight ratio of 25/75 (TPCM/*o*-TP)[15] shows that the Williams–Landel–Ferry (WLF) type free volume[13] holds approximately. The result for pure *o*-TP[16] shows that the configurational entropy and/or internal energy holds, but not the free volume. In order to resolve this discrepancy, we have carried out a similar test on the factors determining molecular mobility in the supercooled liquid of pure TPCM in the present work. We will discuss the intrinsic factor determining mobility in molecular liquids.

Experimental Section

Material. TPCM was purchased from Tokyo Chemical Ind. Co. After repeated recrystallization from methyl alcohol solutions, the single columnar crystals (3 × 4 × 15 mm) were dried under vacuum for several weeks. For differential scanning calorimetry (DSC), the test specimens were cut from the crystals, and for dielectric measurements, the crystals were melted and loaded at 120 °C into the pressure dielectric cell. The supercooled liquid state of the sample thus prepared in the test tube is stable at room temperature over a month.

It should be noted that the materials for the previous studies on the mixture TPCM/*o*-TP (25/75)[15,17,18] are not the same as

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