Thermodynamic efficiency of thermoacoustic mixture separation

D. A. Geller and G. W. Swift
Condensed Matter and Thermal Physics Group, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 1 March 2002; revised 15 May 2002; accepted 21 May 2002)

The acoustic power loss in the thermoacoustic mixture-separation process is derived, including the contributions due to a nonzero gradient in concentration. The significance of the gradient-dependent term is discussed. The limiting thermodynamic efficiency of the separation is calculated. Under reasonable circumstances, the efficiency approaches $10^{-2}n_H n_L(\Delta m/m_{\mathrm{avg}})^2$, where n_H and n_L are the mole fractions of the two components of the mixture, and $\Delta m/m_{\mathrm{avg}}$ is the fractional difference between the molar masses of the two components. This efficiency is of the same order of magnitude as that of some other, more conventional separation methods. © *2002 Acoustical Society of America.* [DOI: 10.1121/1.1494446]

PACS numbers: 43.35.Ud, 43.35.Ty [RR]

I. INTRODUCTION

For 20 years, the field of thermoacoustics has been loosely oriented around the problems of energy conversion in engines and refrigerators.[1] With the discovery of thermoacoustic mixture separation,[2–4] though, another energy-related aspect of thermoacoustics has emerged.

Sound waves in a binary gas mixture in a duct can cause separation of the mixture because the quasiadiabatic temperature oscillation in the bulk of the gas alternately drives each component of the mixture toward the isothermal wall of the duct through thermal diffusion. Then, whichever component has migrated into the boundary layer is trapped there by viscosity during the ensuing motion of the gas. This cycle of thermal diffusion and viscous motion causes the time-averaged net flow of the mixture components in opposite directions along the duct. Thermoacoustic mixture separation is thus intrinsically thermodynamically irreversible, because it is based on two diffusive processes. Ordinary mass diffusion, which is present in all other statistical separation processes as well, is an additional source of irreversibility.

Research and industry have myriad needs to separate mixtures. Whether thermoacoustics can play a meaningful role in this arena depends in part on the thermodynamic efficiency of the thermoacoustic mixture-separation process, which we consider in this paper. First, we derive the full expression for the acoustic power loss to first order in the concentration gradient. We show that the deviation of this loss from the ordinary thermal and viscous dissipative losses is generally very small. The implications of this result for the functioning of thermoacoustic engines and refrigerators are briefly discussed. Next, we derive expressions for the thermodynamic efficiency of thermoacoustic separation in various circumstances. Relative to the fundamental limit imposed by the first and second laws of thermodynamics, the efficiency is only 0.0023 for a 50–50 He–Ar mixture. It is even lower when the components of the mixture are more nearly equal in mass or less equal in concentration. Nevertheless, the efficiency of thermoacoustic mixture separation is actually of the same order of magnitude as that of other widely used irreversible separation processes. Hence, thermoacoustic mixture separation is *not* hopelessly inefficient. Other features, such as simplicity, reliability, low fabrication cost, ability to operate at ambient temperature and pressure, and independence of gravity might make this technique useful for some applications.

II. CALCULATION OF THE DISSIPATION

In order to assess the efficiency of thermoacoustic mixture separation, we first must calculate the rate of acoustic power loss per unit length in the duct. The acoustic loss may not be strictly dissipative, because some of the acoustic power is converted into the free energy of separating the gases. Nevertheless, we expect the dissipation to be substantial, because the separation originates from viscosity and thermal diffusion in the boundary layer, both of which are dissipative processes. To obtain the time-averaged acoustic power loss per unit length, $d\dot{E}_2/dx$, we start from the general formula

$$\frac{d\dot{E}_2}{dx} = -A\frac{d\langle\overline{pu}\rangle}{dx} = -\frac{1}{2}A\Re\left[\langle\tilde{u}_1\rangle\frac{dp_1}{dx} + \tilde{p}_1\frac{d\langle u_1\rangle}{dx}\right], \quad (1)$$

where p_1 and u_1 are the complex amplitudes of oscillating pressure and velocity, respectively, and A is the cross-sectional area of the duct. In our notation,[2,4] $\langle g\rangle$ denotes the average of a quantity g over the cross section of the duct, $\Re[g]$ denotes the real part, $\overline{g}$ denotes the average over time, and $\tilde{g}$ denotes the complex conjugate. The gradient dp_1/dx can be eliminated through the equation for spatially averaged velocity, i.e., the solution of the momentum equation in the acoustic approximation with $u_1 = 0$ at the walls of the duct

$$\frac{dp_1}{dx} = -\frac{\iota\omega\rho_m\langle u_1\rangle}{1-f_\nu}, \quad (2)$$

where ω is the angular frequency, ρ_m is the mean density, and $1-f_\nu$ depends on the profile of velocity on a cross section of the duct and therefore depends on the duct geometry. The gradient of velocity is eliminated using the spatial aver-

 0001-4966/2002/112(2)/504/7/$19.00

age of the equation of continuity to first order in differential quantities

$$\rho_m \frac{d\langle u_1\rangle}{dx} = -\iota\omega\langle \rho_1\rangle - \frac{d\rho_m}{dx}\langle u_1\rangle. \tag{3}$$

Note that we have kept a term in the gradient of the mean density, because for a binary mixture undergoing separation this is not generally zero.

Towards expressing Eq. (1) in terms of $|\langle u_1\rangle|$ and $|p_1|$ alone, without their derivatives, we write the expression for a differential change in the density, following from the ideal gas law

$$\frac{d\rho}{\rho} = \frac{dp}{p} - \frac{dT}{T} + \frac{m_H - m_L}{m_{\text{avg}}} dn_H, \tag{4}$$

where T is the temperature, n_H is the mole fraction of the heavy component, m_H and m_L are the molar masses of the heavy and light components, respectively, and $m_{\text{avg}} = n_H m_H + (1-n_H)m_L$ is the molar average mass. This identity can be used to expand both the first-order oscillating component $\langle \rho_1\rangle$ and the gradient $d\rho_m/dx$ in Eq. (3). As with our earlier derivation of the saturation value of the concentration gradient,[4] we continue to restrict the problem to the case of $dT_m/dx = 0$, and we also assume $dp_m/dx = 0$. Then, Eq. (3) becomes

$$\frac{d\langle u_1\rangle}{dx} = \iota\omega\frac{\langle T_1\rangle}{T_m} - \iota\omega\frac{\gamma}{\rho_m a^2} p_1 - \frac{m_H - m_L}{m_{\text{avg}}}\left(\iota\omega\langle n_1\rangle + \frac{dn_H}{dx}\langle u_1\rangle\right), \tag{5}$$

where a is the sound speed in the mixture, γ is the ratio of specific heats, and we have used the identity $\gamma p_m = \rho_m a^2$. To simplify the final term, we use the single-component continuity equation,[5] which in the present notation is

$$\rho_m\left(\iota\omega\langle n_1\rangle + \frac{dn_H}{dx}\langle u_1\rangle\right) = -\frac{m_{\text{avg}}}{m_H}\langle \boldsymbol{\nabla}\cdot\mathbf{i}_1\rangle \tag{6}$$

to first order, where $\mathbf{i}$ is the diffusive mass-flux density vector. On the right side, $\langle di_{1,x}/dx\rangle$ is negligibly small, and $\langle \boldsymbol{\nabla}_r\cdot\mathbf{i}_1\rangle$ (where r represents the coordinates perpendicular to x) is zero by virtue of the divergence theorem and the boundary condition of zero mass diffusion into the duct wall. Hence, Eq. (5) becomes simply

$$\rho_m\frac{d\langle u_1\rangle}{dx} = \iota\omega\frac{\rho_m}{T_m}\langle T_1\rangle - \iota\omega\frac{\gamma}{a^2}p_1, \tag{7}$$

which is identical to the spatially averaged first-order equation of continuity for a single-component, homogeneous fluid.

For both the boundary-layer limit and for a cylindrical tube of arbitrary diameter, we have shown[4] explicitly that $T_1 = (p_1/\rho_m c_p)(1-h)$, where h is a dimensionless function of the transverse coordinate normal to the wall and c_p is the isobaric specific heat. The first-order equation of continuity can then be rewritten, using the identity $\gamma - 1 = a^2/Tc_p$, as

$$\rho_m a^2\frac{d\langle u_1\rangle}{dx} = -\iota\omega[1 + (\gamma-1)\langle h\rangle]p_1. \tag{8}$$

Substituting Eqs. (2) and (8) into (1), the dissipation is

$$\frac{d\dot{E}_2}{dx} = -\frac{\omega A}{2}\Im\left[\frac{\rho_m|\langle u_1\rangle|^2}{1-f_\nu}\right] - \frac{\omega A}{2}\Im\left[\frac{(\gamma-1)\langle h\rangle|p_1|^2}{\rho_m a^2}\right], \tag{9}$$

where $\Im[g]$ denotes the imaginary part of g.

Consider the two terms in brackets separately. The first term is

$$\frac{\omega A}{2}\frac{\rho_m|\langle u_1\rangle|^2}{|1-f_\nu|^2}\Im[-f_\nu], \tag{10}$$

which is just the ordinary viscous damping term, as noted in Ref. 2. The second term must describe the other diffusive losses (both thermal and mass diffusion) plus the useful work done in separating the components of the mixture. Using Eq. (30) from Ref. 4 for T_1, and with $f_i = \langle h_i\rangle$, we have

$$-\frac{\omega A}{2}\frac{(\gamma-1)|p_1|^2}{\rho_m a^2}\Im[\langle h\rangle] = -\frac{\omega A}{2}\frac{(\gamma-1)|p_1|^2}{\rho_m a^2}\Im[Bf_\nu + Cf_{\kappa D} + (1-B-C)f_{D\kappa}], \tag{11}$$

where the dimensionless coefficients B and C are defined as in Ref. 4 for either the boundary-layer limit or for the case of an arbitrary-diameter tube.

Equations (10) and (11) are still general expressions for the two terms in Eq. (9). To make further progress, we now proceed explicitly in the boundary-layer limit. In that case $f_i = (1-\iota)\delta_i/2r_h$, where r_h is the hydraulic radius.[6] Expression (10) becomes

$$\frac{\omega A}{4r_h}\rho_m|\langle u_1\rangle|^2\delta_\nu. \tag{12}$$

From Ref. 4 we recall

$$B = \frac{\iota e^{-\iota\theta}\varepsilon}{1-f_\nu}\frac{\sigma}{(1-\sigma)(1-\sigma L) - \varepsilon\sigma}\Gamma_c, \tag{13}$$

$$C = C_{\text{S\&S}}\left[1 - B\left(1 + \frac{\sigma-1}{\sqrt{\sigma}}\frac{\delta_\kappa}{\sqrt{L}\delta_{\kappa D} - \delta_{D\kappa}}\right)\right], \tag{14}$$

$$C_{\text{S\&S}} = \frac{\sqrt{L}\delta_{\kappa D} - \delta_{D\kappa}}{(1+\sqrt{L})(\delta_{\kappa D} - \delta_{D\kappa})}, \tag{15}$$

where

$$\Gamma_c = \frac{dn_H/dx}{(dn_H/dx)_{\text{sat}}}, \tag{16}$$

$$\left(\frac{dn_H}{dx}\right)_{\text{sat}} \equiv \frac{\gamma-1}{\gamma}k_T\frac{|p_1|}{p_m}\frac{\omega}{|\langle u_1\rangle|}. \tag{17}$$

In these definitions, k_T is the thermal diffusion ratio, $\varepsilon = (\gamma-1)k_T^2/\gamma n_H(1-n_H)$, σ is the Prandtl number, $L = (\delta_\kappa/\delta_D)^2$, the δ_i are penetration depths all defined in Ref. 2 or 4, and θ is the phase angle by which p_1 leads $\langle u_1\rangle$ in time. Insertion of these coefficients in Eq. (11) yields

$$\frac{\omega A}{4r_h}\frac{(\gamma-1)|p_1|^2}{\rho_m a^2}\frac{\sqrt{L}}{1+\sqrt{L}}(\delta_{\kappa D}+\delta_{D\kappa})\times\left[1-\Gamma_c\frac{\varepsilon\sigma(\sin\theta-\cos\theta)}{(1-\sigma)(1-\sigma L)-\varepsilon\sigma}\times\left(1-\frac{1+\sigma\sqrt{L}}{\sqrt{\sigma L}}\frac{\delta_\kappa}{\delta_{\kappa D}+\delta_{D\kappa}}\right)\right] \tag{18}$$

to lowest order in δ/r_h. This expression for the second term of Eq. (9) is similar in form to the expression for the rate of change of acoustic power in a duct due to a longitudinal temperature gradient but ignoring viscosity.[1] Multiplying the prefactor through the square brackets, the first, θ-independent term is just the thermal damping term found previously in Ref. 2, which could have been obtained more rapidly here by setting $\Gamma_c=0$ in Eq. (11) and comparing with Eq. (57) in Ref. 2. The other term depends on both θ and on the concentration gradient through Γ_c. It is proportional to ε, so it is generally small.

The full expression for acoustic power loss can thus be expressed as the sum of three terms in the boundary-layer limit: a viscous term $d\dot{E}_\nu/dx$, a thermal- and diffusion-loss term $d\dot{E}_{\kappa,D}/dx$, and a term due to the concentration gradient, $d\dot{E}_\nabla/dx$. That is,

$$\frac{d\dot{E}_2}{dx}=\frac{d\dot{E}_\nu}{dx}+\frac{d\dot{E}_{\kappa,D}}{dx}+\frac{d\dot{E}_\nabla}{dx}, \tag{19}$$

where

$$\frac{d\dot{E}_\nu}{dx}=\frac{\omega A}{4r_h}\rho_m|\langle u_1\rangle|^2\delta_\nu, \tag{20}$$

$$\frac{d\dot{E}_{\kappa,D}}{dx}=\frac{\omega A}{4r_h}\frac{(\gamma-1)}{\rho_m a^2}|p_1|^2\frac{\sqrt{L}}{1+\sqrt{L}}(\delta_{\kappa D}+\delta_{D\kappa}), \tag{21}$$

$$\frac{d\dot{E}_\nabla}{dx}=\frac{\delta_\kappa}{4r_h}\frac{\gamma-1}{\gamma}\frac{k_T}{n_H(1-n_H)}\frac{dn_H}{dx}\frac{|p_1||U_1|(\cos\theta-\sin\theta)}{(1-\sigma)(1-\sigma L)-\varepsilon\sigma}\times\frac{\sigma\sqrt{L}}{1+\sqrt{L}}\left[\frac{\delta_{\kappa D}}{\delta_\kappa}+\frac{\delta_{D\kappa}}{\delta_\kappa}-\frac{1+\sigma\sqrt{L}}{\sqrt{\sigma L}}\right], \tag{22}$$

with $U_1=A|\langle u_1\rangle|$ the volume flow rate. The new term, $d\dot{E}_\nabla/dx$, must include the reversible work stored in the concentration gradient, but Eq. (18) suggests that $d\dot{E}_\nabla/dx$ be viewed as a correction to the thermal- and mass-diffusion loss accounting for the presence of this gradient. Note that in the limit $k_T\to 0$, we find $d\dot{E}_\nabla/dx\to 0$, and $d\dot{E}_{\kappa,D}/dx$ approaches the well-known boundary-layer thermal-loss term for acoustics alone.

As described in Ref. 4, Watson[7] has also considered mixtures subjected to oscillating flow in ducts, but neglecting thermal diffusion and setting $p_1=0$. Watson took the acoustic dissipation per unit length in a duct to be

$$\frac{d\dot{E}_{\text{Watson}}}{dx}=\Re\left\{\left\langle\tilde{u}_1\frac{dp_1}{dx}\right\rangle\right\}, \tag{23}$$

neglecting the $\tilde{p}_1\,du_1$ portion of the differential acoustic power. As a result, Watson's expressions for the power dissipation are equal only to our expression (10) for the viscous loss. Specifically, Watson's expression (107) for $\omega\to\infty$, which is equivalent to our boundary-layer limit, is exactly equal to our Eq. (20). By discarding the differential $\tilde{p}_1\,du_1$, Watson neglected both the thermal loss and the gradient-dependent loss. Strictly speaking, even if one attempted to keep $p_1=0$ in this situation, the concentration oscillations would drive temperature oscillations (via ε), which in turn could drive density and pressure oscillations, contributing to the gradient-dependent loss. However, we will see in the next section that neglect of this effect is not serious.

III. CONCENTRATION-GRADIENT-DEPENDENT LOSSES

To quantify the relative importance of the new, gradient-dependent term $d\dot{E}_\nabla/dx$, we define the ratio

$$b=\frac{(d\dot{E}_\nabla/dx)}{(d\dot{E}_\nu/dx+d\dot{E}_{\kappa,D}/dx)}, \tag{24}$$

which equals the fractional deviation of the total acoustic loss from the acoustic loss calculated in Ref. 2. This ratio is a function of k_T, T_m, p_m, ρ_m, n_H, ω, r_h, the δ_i, θ, γ, dn_H/dx, $|p_1|$, and $|\langle u_1\rangle|$. However, it is not difficult to show that b is only weakly dependent on most of these parameters, and we can obtain a rough upper limit on this ratio for cases of practical interest.

The ratio b is proportional to the concentration gradient. For any closed system, the highest gradient will occur when the thermoacoustic separation process saturates at $\dot{N}_H=0$. Using Eqs. (41), (44), and (56) from Ref. 4, we can write this limiting value as

$$\left(\frac{dn_H}{dx}\right)_{\text{lim}}=\frac{(F_{\text{trav}}\cos\theta+F_{\text{stand}}\sin\theta)(\gamma-1)k_T|p_1||\langle u_1\rangle|/\gamma p_m}{4D_{12}r_h/\delta_\kappa-F_{\text{grad}}|\langle u_1\rangle|^2/\omega}, \tag{25}$$

where D_{12} is the coefficient of mutual diffusion for the two components of the gas. Although it is experimentally possible to create much higher concentration gradients than this, such gradients must decay rapidly unless streams of unmixed gases are continuously injected into the system. In the context of using thermoacoustics to separate gases which are initially well mixed, we assume that the maximum concentration gradient is this limiting value.

Using Eq. (25) in Eq. (24), we can maximize b in terms of the acoustic amplitudes $|p_1|$ and $|\langle u_1\rangle|$. It is most convenient to replace $|p_1|$ by $z|\langle u_1\rangle|$, where z is the magnitude of the specific acoustic impedance. In that case one finds that b increases asymptotically toward the value

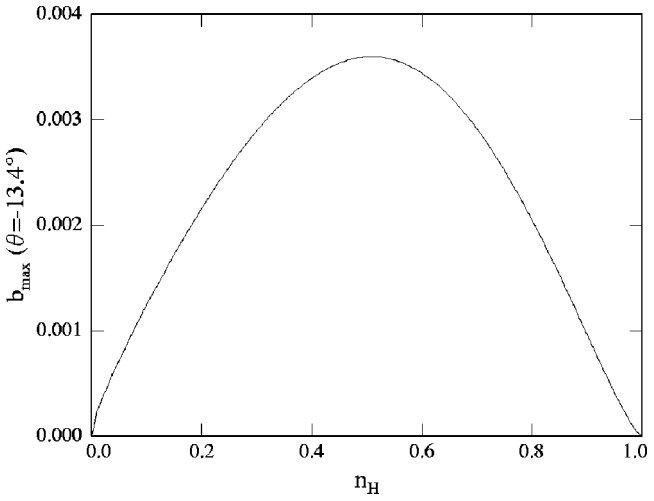

FIG. 1. The maximum ratio of gradient-dependent loss to thermal and viscous losses, for He–Ar mixtures in the boundary-layer limit with $\theta=-13.4°$.

$$b_{\max}=\frac{(F_{\text{trav}}\cos\theta+F_{\text{stand}}\sin\theta)(\sin\theta-\cos\theta)\varepsilon\sigma}{F_{\text{grad}}[(1-\sigma)(1-\sigma L)-\varepsilon\sigma]}\times\left[1-\frac{1+\sigma\sqrt{L}}{\sqrt{\sigma L}}\frac{\delta_\kappa}{\delta_{\kappa D}+\delta_{D\kappa}}\right], \tag{26}$$

as $z\to\infty$ and as $|\langle u_1\rangle|\to\infty$. "Infinite" $|\langle u_1\rangle|$ cannot be approached in reality because the oscillating flow would become turbulent, likely destroying the separation effect. Therefore, we take this limit to imply velocities just below the onset of turbulence. For the He–Ar mixtures studied in Refs. 2–4, $b_{\max}$ is maximized when $\theta\approx-13.4°$. By analogy with Fig. 5 from Ref. 2, we show $b_{\max}$ at $\theta=-13.4°$ as a function of n_H in Fig. 1. Because He–Ar mixtures have among the highest thermal diffusion ratios found in nature, it is unlikely that a $b_{\max}$ much greater than 0.004 will be encountered in any mixture separation.[8,9] Since $d\dot{E}_{\kappa,D}/dx$ differs little[2] from the ordinary thermal loss in a homogeneous gas, we conclude in general that, even with $dn_H/dx\neq0$, the added dissipation caused by thermoacoustic separation is much smaller than the ordinary thermal and viscous losses which would be calculated assuming a pure gas.

It is fortunate that $b_{\max}$ is small. If the acoustic dissipation arising from the concentration gradient had turned out to be large, then we would have to reformulate much of thermoacoustics: Rott's equations[10] assume a simple, nonseparable gas, and hence do not strictly apply to the propagation of sound in mixtures. Because $d\dot{E}_\nabla/dx$ is generally much smaller than the other acoustic losses, though, and because $d\dot{E}_{\kappa,D}/dx$ typically differs from the pure-gas thermal dissipation by less than 1%,[2] Rott's equations accurately describe the local properties of most thermoacoustic engines and refrigerators in practice. There are at least two important exceptions. First, the mixture-separation phenomenon can easily create a spatial distribution of the gas composition, and hence a significant x dependence of the gas properties that must be used in Rott's equations. This fact is illustrated by the resonator coupling experiment[2] in which the separation effect was discovered. Second, dramatic changes to the equations of thermoacoustics result when one component of the mixture experiences evaporation and liquefaction in the acoustic process.[11]

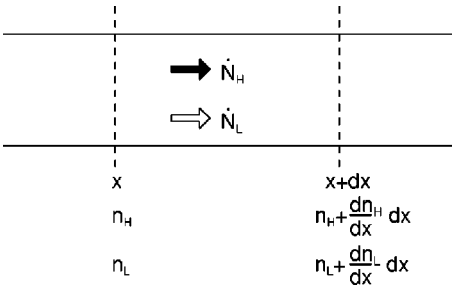

FIG. 2. Sign conventions used to derive the increase in Gibbs free energy associated with mixture separation along a duct. For the process considered here, we have $\dot{N}_L=-\dot{N}_H$, $n_L=1-n_H$, and $dn_L/dx=-dn_H/dx$.

Finally, because dn_H/dx can have either sign, the concentration gradient seems to offer the possibility of creating or amplifying sound, much like the temperature gradient across the stack or regenerator in a thermoacoustic engine, and it is interesting to consider whether such mixing-driven acoustic power production could be experimentally demonstrated. Unfortunately, $d\dot{E}_\nabla/dx$ is overwhelmed by the ordinary viscous and thermal dissipation unless the concentration gradient is extremely abrupt. We have not discovered a way to demonstrate this effect.

IV. THERMODYNAMIC EFFICIENCY

We can define the efficiency of thermoacoustic separation by the ratio of the rate at which useful separation work is done to the total acoustic power consumed in performing the separation

$$\eta=\frac{d\dot{G}/dx}{d\dot{E}_{\text{tot}}/dx}, \tag{27}$$

where $d\dot{G}/dx$ is the rate at which the Gibbs free energy of the mixture increases, per unit length. This definition of efficiency is thermodynamically meaningful, because $\dot{G}$ is the rate at which exergy (i.e., useful work) is built up in the separating mixture[12] and $\dot{E}_{\text{tot}}$ is the rate at which exergy is consumed by the wave[13] if the duct walls are in contact with a thermal reservoir at a temperature at which heat has no value.

We can derive a simple expression for $d\dot{G}/dx$ by starting with the well-known[14] concentration contribution to the free energy of a *homogeneous* binary mixture of N total moles

$$G=NR_{\text{univ}}T_m(n_H\log n_H+n_L\log n_L). \tag{28}$$

As illustrated in Fig. 2, the length dx of the thermoacoustic separation duct moves $\dot{N}_H\,dt$ moles of the heavy component from a location where the concentration is n_H to one where the concentration is $n_H+(dn_H/dx)dx$, and similarly moves $\dot{N}_L\,dt$ moles of the light component from n_L to $n_L+(dn_L/dx)dx$. The change in G for this process is

$$d^2G = R_{\text{univ}} T_m \Big[\dot{N}_H \, dt \log\Big(n_H + \frac{dn_H}{dx} dx \Big) - \dot{N}_H \, dt \log n_H + \dot{N}_L \, dt \log\Big(n_L + \frac{dn_L}{dx} dx \Big) - \dot{N}_L \, dt \log n_L \Big]. \tag{29}$$

Combining the logarithms and using the identities given in the caption of Fig. 2 quickly yields

$$\frac{d\dot{G}}{dx} = \frac{R_{\text{univ}} T_m}{n_H(1-n_H)} \frac{dn_H}{dx} \dot{N}_H, \tag{30}$$

where $\dot{N}_H$ is the mole flux of the heavy component. Using Eqs. (41), (44), and (56) from Ref. 4 for the mole flux through second order, this may be rewritten as

$$\frac{d\dot{G}}{dx} = \frac{1}{n_H(1-n_H)} \frac{dn_H}{dx} \Big[\frac{\delta_\kappa}{4r_h} \frac{\gamma-1}{\gamma} k_T |p_1| \times |U_1| (F_{\text{trav}} \cos\theta + F_{\text{stand}} \sin\theta) + \frac{\delta_\kappa}{4r_h} \frac{p_m}{\omega A} F_{\text{grad}} |U_1|^2 \frac{dn_H}{dx} - p_m A D_{12} \frac{dn_H}{dx} \Big]. \tag{31}$$

Although $\dot{G}$ and $\dot{E}_\nabla$ are both powers associated with separating the mixture along a concentration gradient, they differ dramatically. Whereas Eq. (22) is linear in the concentration gradient, Eq. (31) is quadratic in dn_H/dx. The term linear in dn_H/dx is quite similar to $d\dot{E}_\nabla/dx$, but it differs in its phase dependence and its lack of the combinations of L, σ, $\delta_{D\kappa}$, and $\delta_{\kappa D}$ appearing in Eq. (22). Moreover, while $d\dot{G}/dx \to 0$ as the separation approaches saturation, $d\dot{E}_\nabla/dx$ does not generally vanish, and if one first establishes a concentration gradient and then turns off the acoustics, $d\dot{E}_\nabla/dx = 0$ while $d\dot{G}/dx$ gives a nonzero energy loss as the concentration gradient decays by ordinary diffusion. Hence, $d\dot{E}_\nabla/dx$ must describe not only energy transferred from the acoustic wave into separation of the gases but also more subtle features of the dissipation which are lost in the heuristic description of separation given in Ref. 2. For example, while Eq. (21) describes losses due to diffusion of heat and of mass at the boundary layer and driven by the oscillating temperature T_1 when $dn_H/dx = 0$, this loss must be adjusted higher or lower by Eq. (22) in the presence of a longitudinal concentration gradient. This adjustment depends not only on the gradient but on the phasing of the acoustic fields, because the enhancement or depletion of one species outside the boundary layer will lead to either more or less thermal diffusion radially, depending on whether the motion is in phase or out of phase with respect to the temperature oscillations.

In the denominator of Eq. (27) we could use Eq. (19). However, Sec. III above and Sec. V of Ref. 2 show that, to a high degree of accuracy, we can ignore all the contributions to acoustic dissipation arising from thermal diffusion and simply use the ordinary expression for the acoustic dissipation

$$\frac{d\dot{E}_{\text{tot}}}{dx} \approx \frac{\omega A}{4r_h} \rho_m |\langle u_1 \rangle|^2 \delta_\nu + \frac{\omega A}{4r_h} \frac{\gamma-1}{\rho_m a^2} |p_1|^2 \delta_\kappa, \tag{32}$$

yielding some immediate simplification.

For comparison with other separation methods, it is necessary to find the conditions that maximize η. In particular, one must determine at what concentration gradient the maximum η occurs. Since neither of the terms in (32) depends on dn_H/dx, the maximum efficiency must occur when $d\dot{G}/dx$ is itself a maximum. Equation (31) shows that this rate is quadratic in dn_H/dx, and it is straightforward to show that the only maximum occurs when

$$\frac{dn_H}{dx} = \frac{1}{2} \Big(\frac{dn_H}{dx} \Big)_{\text{lim}}, \tag{33}$$

where $(dn_H/dx)_{\text{lim}}$ is the value of dn_H/dx for which $\dot{N}_H = 0$, obtained in Eq. (25). (Because effects which remix the gases, such as ordinary diffusion, enter the expression for the mole flux $\dot{N}_H$ at first order in dn_N/dx for many other thermophysical separation processes as well, the maximum rate at which useful separative work can be done often occurs when the concentration gradient is at half of its saturation value.[15]) Inserting this gradient into Eq. (31), and using Eq. (32), we obtain the efficiency at the best dn_H/dx

$$\eta(\text{best } dn_H/dx) = \frac{(\gamma-1)^2 k_T^2 (z')^2 (F_{\text{trav}} \cos\theta + F_{\text{stand}} \sin\theta)^2}{4\gamma n_H(1-n_H)[(\gamma-1)(z')^2 + \sqrt{\sigma}](-F_{\text{grad}} + 4D_{12}\omega r_h/\delta_\kappa |\langle u_1 \rangle|^2)}, \tag{34}$$

where $z' = |p_1|/\rho_m a |\langle u_1 \rangle|$. This efficiency is maximized asymptotically as $z' \to \infty$ and as $|\langle u_1 \rangle| \to \infty$, where $|\langle u_1 \rangle|$ again must be kept below the onset of turbulence. The only other adjustable parameter is the wave's phasing θ. To maximize the efficiency with respect to θ, $\tan\theta = F_{\text{stand}}/F_{\text{trav}}$, so that the limiting efficiency for thermoacoustic separation is finally

$$\eta_{\text{best}} = \frac{\varepsilon}{4} \frac{F_{\text{trav}}^2 + F_{\text{stand}}^2}{-F_{\text{grad}}}. \tag{35}$$

In the context of Refs. 2–4, $\eta_{\text{best}} = 0.0023$ for a 50–50 He–Ar mixture.

Taking $\varepsilon \ll 1$ leads to great simplification in the three

F's in Eq. (35), so that in this limit the best thermoacoustic efficiency becomes

$$\eta_{\mathrm{ta,best}} \approx \frac{\varepsilon}{4} \frac{2(1+\sqrt{\sigma L})}{\sqrt{L}(1+\sqrt{L})^2(1+\sigma)}. \tag{36}$$

We will compare this expression to the efficiencies of other mixture-separation methods in the next section.

In practice, it is easy to achieve values of dn_H/dx, z', $|\langle u_1 \rangle|$, and θ that bring η close to $\eta_{\mathrm{ta,best}}$. For example, some of the measurements reported in Ref. 4 had θ at its optimum value, $z' \approx 4$, and $|\langle u_1 \rangle|$ large enough to make $4D_{12}\omega r_h/\delta_\kappa |\langle u_1 \rangle|^2(-F_{\mathrm{grad}}) \approx 0.02$. At some time during the approach to the saturation data reported in Ref. 4, Eq. (33) was satisfied as well. Under these circumstances, $\eta/\eta_{\mathrm{ta,best}} \approx 0.9$.

V. COMPARISON TO TRADITIONAL METHODS

Mixture-separation methods can be broadly divided into two categories, those that are intrinsically reversible and those that are intrinsically irreversible. The use of perfect semipermeable membranes is an example of an intrinsically reversible separation method; for example, helium and hydrogen can be separated from much heavier gases using such membranes, with a thermodynamic efficiency near unity. Distillation separation methods[16,17] (e.g., air-separation plants) are also impressively efficient, often exceeding $\eta = 0.5$ in industrial practice. Relying as it does on intrinsically irreversible processes—diffusion of heat, mass, and momentum—thermoacoustic mixture separation cannot approach these high efficiencies.

However, many important mixtures, including those of most isotopes and of most isomers, must be separated by intrinsically irreversible methods, because the more efficient methods are inapplicable. The intrinsically irreversible methods include traditional thermal diffusion, gaseous diffusion, and mass diffusion.[18] To get an initial impression of how the efficiency of thermoacoustic mixture separation compares with those of these other methods, we will focus on isotope separation and on the first two intrinsically irreversible methods listed above.

The very process of thermal diffusion was only discovered between 1911 and 1917,[19] and attempts to separate isotopes with it followed quickly, with Clusius and Dickel[20] separating neon isotopes in 1938. Their apparatus comprised two vertical concentric tubes, the inner one heated and the gas mixture between the two. Thermal diffusion draws the lighter isotope toward the inner tube, and the heavier toward the outer tube, so that gravity-driven convection separates them vertically.

While thermal diffusion was discovered as a consequence of the kinetic theory of gases, the origins of gaseous diffusion are much older, tracing back to the experiments of Graham in the mid-19th century on the effusion of gases through porous materials. Although gaseous diffusion was used in the discoveries of the noble gases at the end of the 19th century, it was not until 1920 that the process was used for an isotope separation, in neon.[21] In a gaseous-diffusion system, the gas mixture is supplied at a constant pressure to one side of a porous barrier which is held at lower pressure on the other side. If the pore size is small enough, gas moves through the pores in Knudsen flow, and the components of the mixture escape to the low-pressure side at rates inversely proportional to the square root of their molecular masses.

Onsager[22] derived fundamental bounds on the efficiencies of separations based on thermal diffusion and gaseous diffusion. Our derivation of Eq. (30) is similar to his, and he further argued that the exergy spent in thermal-diffusion separation must be at least as large as the exergy lost in thermal conduction through the gas, and the exergy spent in gaseous-diffusion separation must be at least as large as the exergy dissipated in the free expansion. In our notation, his results are

$$\eta_{\mathrm{td,best}} = \frac{\varepsilon}{4}\frac{1}{L}, \tag{37}$$

$$\eta_{\mathrm{gd,best}} = \frac{n_H(1-n_H)}{4}\left(\frac{\Delta D}{D}\right)^2, \tag{38}$$

where D is the average gas diffusion constant, ΔD is the difference between the Ds for the two components of the gas, and the subscripts td and gd signify thermal diffusion and gaseous diffusion, respectively. Note the obvious similarity between Eqs. (35) and (37). For a 50–50 He–Ar mixture, these equations show that $\eta_{\mathrm{best}} = 0.57\,\eta_{\mathrm{td,best}}$.

To make further progress in approximately comparing the efficiencies of thermoacoustic, thermal-diffusion, and gaseous-diffusion separation, we will make some estimates using the hard-sphere kinetic-theory values[16,23] of the various parameters, assuming that the molar mass difference $\Delta m = m_H - m_L$ is much smaller than m_{avg}

$$\gamma = \tfrac{5}{3}, \quad \sigma = \tfrac{2}{3}, \quad L = \tfrac{5}{4}, \tag{39}$$

$$k_T = n_H(1-n_H)\frac{105}{236}\frac{\Delta m}{m_{\mathrm{avg}}}, \tag{40}$$

$$\frac{\Delta D}{D} = \frac{\Delta m}{2m_{\mathrm{avg}}}. \tag{41}$$

With these values, Eqs. (36), (37), and (38) become

$$\eta_{\mathrm{ta,best}} = 0.009 n_H(1-n_H)(\Delta m/m_{\mathrm{avg}})^2, \tag{42}$$

$$\eta_{\mathrm{td,best}} = 0.016 n_H(1-n_H)(\Delta m/m_{\mathrm{avg}})^2, \tag{43}$$

$$\eta_{\mathrm{gd,best}} = 0.063 n_H(1-n_H)(\Delta m/m_{\mathrm{avg}})^2. \tag{44}$$

Remarkably, these are all of the same order of magnitude, and share the same dependence on concentration and mass difference.

As an example of an economically important, intrinsically irreversible separation, consider the enrichment of uranium.[24] Most commercial power reactors use uranium that has been enriched by gaseous diffusion of UF_6 to about 3% U^{235}; the natural abundance is 0.7%. Evaluation of Eq. (44) for this situation yields $\eta_{\mathrm{gd,best}} \approx 10^{-7}$. The Tricastin (France) uranium enrichment facility actually operates at an efficiency of 10^{-8}. This example merely demonstrates that an extremely inefficient separation process can nevertheless

be important. In considering possible applications of thermoacoustic mixture separation, the intrinsic thermodynamic efficiency is not prohibitively low, so issues such as cost and reliability might be decisive.

ACKNOWLEDGMENTS

This work was supported by the Division of Materials Sciences in the U.S. Department of Energy's Office of Science.

[1] G. W. Swift, ''Thermoacoustic engines,'' J. Acoust. Soc. Am. **84**, 1145–1180 (1988).
[2] G. W. Swift and P. S. Spoor, ''Thermal diffusion and mixture separation in the acoustic boundary layer,'' J. Acoust. Soc. Am. **106**, 1794–1800 (1999); **107**, 2299(E) (2000); **109**, 1261(E) (2001).
[3] P. S. Spoor and G. W. Swift, ''Thermoacoustic separation of a He–Ar mixture,'' Phys. Rev. Lett. **85**, 1646–1649 (2000).
[4] D. A. Geller and G. W. Swift, ''Saturation of thermoacoustic mixture separation,'' J. Acoust. Soc. Am. **111**, 1675–1684 (2002).
[5] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, New York, 1982), Eq. (57.3).
[6] The hydraulic radius r_h of a duct is defined as the ratio of the cross-sectional area to the perimeter. For a right circular cylinder, the hydraulic radius is equal to one half of the cylinder radius.
[7] E. J. Watson, ''Diffusion in oscillating pipe flow,'' J. Fluid Mech. **133**, 233–244 (1983).
[8] Note that in the above expression, the δ_i enter only in ratios. The mass diffusion coefficient D_{12}, the kinematic viscosity ν, and the thermal diffusivity κ are all proportional to $1/\rho$ and therefore to $1/p$. Furthermore, each of these parameters has approximately the same weak power-law dependence on temperature; in the simplest mean-free-path theory for a dilute gas of rigid spheres, this power law is $\sqrt{T}$. Thus, ratios of the δ_i, such as σ and L, are essentially independent of pressure and roughly independent of temperature in the regime that the gases in the mixture can be considered ideal. See Ref. 23.
[9] In general, k_T can be a function of both temperature and pressure. The temperature dependence typically exhibits a maximum value (at fixed pressure), and for the room-temperature He–Ar mixtures of our previous experiments, k_T is 0.8 of its maximum value at atmospheric pressure. The experimentally measured k_T may either increase or decrease with pressure, but this effect is due to the nonidealities in the equations of state of the gases. See K. E. Grew and T. L. Ibbs, *Thermal Diffusion in Gases* (Cambridge University Press, Cambridge, 1952), Chaps. 4–5. Nonideal gas behavior is beyond the scope of our treatment.
[10] N. Rott, ''Damped and thermally driven oscillations in wide and narrow tubes,'' Z. Angew. Math. Phys. **20**, 230–243 (1969), and N. Rott, ''Thermally driven oscillations. III. Second-order heat flux,'' *ibid.* **26**, 43–49 (1975).
[11] R. Raspet, C. J. Hickey, and J. M. Sabatier, ''The effect of evaporation-condensation on sound propagation in cylindrical tubes using the low reduced frequency approximation,'' J. Acoust. Soc. Am. **105**, 65–73 (1999); W. V. Slaton and R. Raspet, ''Wet-walled thermoacoustics,'' *ibid.* **110**, 2677 (2001); William V. Slaton, ''Inert gas–vapor mixtures in thermoacoustics,'' Ph.D. thesis, University of Mississippi, 2001.
[12] A. Bejan, *Advanced Engineering Thermodynamics*, 2nd ed. (Wiley, New York, 1997).
[13] G. W. Swift, *Thermoacoustics: A Unifying Perspective for Some Engines and Refrigerators*, Chap. 6 (Acoustical Society of America, 2002)
[14] This can be found in many introductory thermodynamics texts. For example, see Eqs. (4.128) and (4.139) in Ref. 12.
[15] H. London, *Separation of Isotopes* (Newnes, London, 1961).
[16] S. Villani, *Isotope Separation* (American Nuclear Society, La Grange Park, IL, 1976).
[17] *Encyclopedia of Separation Technology*, edited by D. M. Ruthven (Wiley, New York, 1997), Vol. 1.
[18] Gaseous diffusion describes effusion, or the molecular flow of a gas through narrow pores into vacuum. In mass diffusion, the mixture is separated by the difference in the components' rates of diffusion through a carrier gas (preferably one which is easily stripped from the product). See Ref. 16 for details of these methods.
[19] For an account of the theoretical discovery by Enskog and Chapman separately, and the experimental confirmation by Chapman and Dootson, see the review by R. Clark Jones, and W. H. Furry, ''The separation of isotopes by thermal diffusion,'' Rev. Mod. Phys. **18**, 151–224 (1946).
[20] K. Clusius and G. Dickel, ''Neues Verfahren zur Gasentmischung und Isotopentrennung,'' Naturwissenschaften **26**, 546(L) (1938).
[21] D. Massignon, in *Topics in Applied Physics: Uranium Enrichment*, edited by S. Villani (Springer, New York, 1979), Vol. 35, pp. 55–56.
[22] L. Onsager, ''Separation of gas (isotope) mixtures by irreversible processes,'' Phys. Rev. **55**, 1137(A) (1939).
[23] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).
[24] Anthony V. Nero, *Guidebook to Nuclear Reactors* (University of California Press, Berkeley, 1979); see also the Uranium Information Centre at www.uic.com.au.