Rayleigh-Bénard convection in binary-gas mixtures: Thermophysical properties and the onset of convection

Jun Liu and Guenter Ahlers

Department of Physics and Center for Nonlinear Science, University of California, Santa Barbara, California 93106

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We present an experimental investigation of Rayleigh-Bénard convection in binary-gas mixtures. In order to interpret the results quantitatively, we determined the necessary thermodynamic and transport properties for six mixtures (He-CO\textsubscript{2}, He-SF\textsubscript{6}, He-Xe, Ne-Ar, Ar-CO\textsubscript{2}, and H\textsubscript{2}-Xe) by a combination of data from the literature, molecular-theory calculations, and thermal-conductivity measurements. All six mixtures have positive separation ratios $\Psi$. The Lewis number $L$ (the ratio of the mass to the thermal diffusivity) is of $O(1)$, in contrast to liquid mixtures where $L=O(10^{-5})$. An important feature of the gas mixtures is that their Prandtl number (the ratio of the kinematic viscosity to the thermal diffusivity) can be lower than those of the two pure components.

We discuss the physical reason for this and show that the minimum Prandtl number reached by using binary-gas mixtures is about 0.16. The critical temperature difference $\Delta T_c$ for the onset of convection is determined from measurements of the Nusselt number $N$ (the effective thermal conductivity) and from the contrast of shadowgraph images as a function of $\Delta T$. The results agree well with the prediction of linear stability analysis. In contrast to convection in binary-liquid mixtures with $\Psi>0$, $N$ for the gas mixtures increases significantly with $\epsilon=\Delta T/\Delta T_c-1$ as soon as the convection starts at the Soret onset and is qualitatively similar to the Nusselt number of pure fluids. However, the critical Rayleigh number $R_c$ is lower than the value $R_{c0}=1708$ of pure fluids. The pattern at onset in the gas mixtures initially consists of parallel straight rolls, in contrast to binary-liquid mixtures where the pattern consists of squares. Based on the gas-mixture properties, we find that the Dufour effect (the reciprocal process of the Soret effect) is relatively weak. The slope $dN/d\epsilon$ of $N$ at onset is found to be consistent with that predicted by an eight-mode Galerkin truncation. [S1063-651X(97)04206-2]

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I. INTRODUCTION

A quiescent horizontal fluid layer heated from below becomes unstable and undergoes a transition to buoyancy-driven convection, namely, Rayleigh-Bénard convection (RBC), when the temperature difference $\Delta T$ across it exceeds a critical value $\Delta T_c$. This system has long been used to investigate many fundamental and practical problems [1–8]. Particularly, it has become a paradigm in the study of complex spatiotemporal behavior in spatially extended nonequilibrium systems [6]. This is so for two reasons. On the one hand, RBC lends itself to well controlled, quantitative experiments [5,8]. On the other hand, the equations of motion of the system are well known (the Navier-Stokes equations and associated boundary conditions) and permit a close connection between theory and experiment, which has led to detailed tests of theoretical concepts [2,3,6]. There has been a large amount of experimental work on RBC in single-component liquids and gases and in binary-liquid mixtures. In this paper, we report RBC experiments in binary-gas mixtures and show that they open an alternative parameter range with different opportunities in the study of RBC.

The primary control parameter for RBC is the Rayleigh number

$$R = \frac{\alpha gd^3 \Delta T}{\kappa \nu},$$

a dimensionless measure of the temperature difference across the fluid layer. Here

$$\alpha = -\frac{(1/p)(\partial p/\partial T)}{P},$$

is the isobaric thermal expansion coefficient ($p$ is the density and $P$ the pressure), $g$ the acceleration of gravity, $d$ the fluid-layer thickness, $\kappa$ the thermal diffusivity, and $\nu$ the kinematic viscosity. As $R$ increases from zero, the destabilizing density gradient (or buoyancy force) increases. Convection occurs when $R$ exceeds a critical value $R_c$ ($\Delta T$ exceeds $\Delta T_c$). For a single-component fluid, the critical Rayleigh number (corresponding to $\Delta T=\Delta T_{c0}$) is $R_{c0}=1708$, independent of material properties, and the convection just above onset consists of stationary rolls. When $R$ increases further above $R_{c}$, various flow patterns and time dependences evolve [5,9–12], and turbulence appears at very large $R$ [7].

The nonlinear behavior of convection above $R_c$ depends on the Prandtl number

$$\sigma = \nu/\kappa$$

as well as on $R$. Although $\sigma$ does not affect the onset of convection, it has important effects on secondary instabilities of the convection-roll patterns. For the idealized case of infinitely extended parallel straight rolls, Busse and collaborators [2,13–15] have determined the main features of these instabilities as well as their boundaries as a function of $R$, $\sigma$, and the roll wave number $k$. These predictions describe fairly well also the case of convection in large but finite samples when $\sigma$ is large. However, for low $\sigma$ experiments have revealed complex spatiotemporal behavior at $R$ slightly above $R_c$ [5,12,16–18], where straight rolls are predicted to...
be stable in the infinite system. To a large extent this time
dependence of the patterns is associated with roll curvature
induced by the sidewalls of the cell, which leads to large-
scale flows. These flows in turn create a wave-number dis-
tribution that, for small $\sigma$, overlaps the stability boundaries
of the infinite system [5,12].

Another parameter relevant to experiments is the lateral
extent of a convection cell, as described by the aspect ratio

$$\Gamma = r/d,$$  \hspace{1cm} (4)

where $r$ is the radius for a cylindrical cell. When the system
is small ($\Gamma \leq 3$), RBC can exhibit temporal chaos [6,19,20]
as $R$ increases from $R_c$, and the spatial dependence is dy-
namically unimportant. For large $\Gamma$, the spatial degrees of
freedom play an important role in the complex evolution of
convection patterns, resulting in spatiotemporal chaos
[5,17,18,21–24]. Recently it was shown that the onset of
spiral-defect chaos, a spatiotemporal chaos occurring only
for $\Gamma > 1$ and low $\sigma$, depends significantly on the aspect ratio
[17,18,23,25].

The nature of Rayleigh-Bénard convection in pure fluids
is determined by the above three dimensionless numbers
when the Oberbeck-Boussinesq approximation [26–28] ap-
plies. In this approximation it is assumed that the variations
of all fluid properties with temperature (except for the den-
sity in the buoyancy force) can be neglected. For most of the
work reported in this paper this approximation is very good.

For binary mixtures, additional parameters are required to
describe the nature of the convection state because of the
interaction between concentration and temperature fields. This
coupling results in new phenomena that do not occur in pure
fluids, including traveling waves, localized pulses, time-
dependent envelopes of the convection rolls, and square pat-
tens [29–31]. In binary mixtures, temperature gradients
change the concentration field because of thermal diffusion
[32,33]. This so-called Soret effect is characterized in RBC
by the separation ratio

$$\Psi = - \frac{\beta}{\alpha} \left( \frac{k_T}{T} - \frac{\beta}{\alpha} (1-C) S_T \right),$$  \hspace{1cm} (5)

where $\beta$ is the solutal expansion coefficient, $k_T$ the thermal
diffusion ratio [34], $T$ the temperature, $C$ the mass concen-
tration of the heavier component [see Eq. (14) below], and
$S_T = k_T/C(1-C)T$ the Soret coefficient. The quantity $k_T$
is defined so that the heavier component moves to the cold
(hot) region when $k_T > 0$ ($k_T < 0$). The thermal expansion
coefficient $\alpha$ [Eq. (2)] is computed at constant $C$ and

$$\beta = -(1/p) (\partial p/\partial C)_{P,T}. \hspace{1cm} (6)$$

When $\Psi < 0$, the induced concentration gradient stabilizes
the conduction state because the heavy component moves to
the hot region and retards the buoyancy. Thus the critical
Rayleigh number is elevated, i.e., $R_c > R_{c0}$. On the other
hand, when $\Psi > 0$, the induced concentration gradient is
destabilizing the conduction state and the critical Rayleigh
number is reduced, i.e., $R_c < R_{c0}$.

In binary mixtures, the dynamics of the concentration
variable is associated with an independent time scale gov-
erned by the concentration diffusivity $D$. Thus the Lewis
number

$$\mathcal{L} = D/\kappa$$  \hspace{1cm} (7)

is an important parameter that measures the ratio of the
thermal-diffusion time to the mass-diffusion time. For liquid
mixtures, $\mathcal{L}$ is small [$\mathcal{O}(10^{-2})$]. In that case it is possible for
the convection to temporarily lag behind the thermal gra-
dient. When $\Psi < 0$, this can lead to oscillations that are re-
 sponsible for the existence of traveling waves and other in-
teresting phenomena [29]. On the other hand, for $\Psi > 0$, the
convection is stationary and the pattern that forms for small
$\mathcal{L}$ is one of squares [30,31,35]. Mass diffusion carries little
heat for small $\mathcal{L}$ and thus for $\Psi > 0$ the heat transport is not
significantly enhanced by the convection for $R_c < R < R_{c0}$
[30,31], where the Soret mechanism dominates. In binary-
 gas mixtures, however, $\mathcal{L} = \mathcal{O}(1)$ and the heat transport is
enhanced significantly in the range $R_c < R < R_{c0}$, as we will
show in this paper. The pattern immediately above $R_c$ then
consists of rolls like those in pure fluids.

The coupling of temperature and concentration in binary
mixtures also gives rise to the Dufour effect, which consists
of temperature gradients induced by concentration gradients.
It is the reciprocal process of the Soret effect in Onsager’s
linear reciprocal relations [32,36,37]. Recently, Lücke and
co-workers [37,38] carried out a theoretical study of the role
of the Dufour effect in RBC. A dimensionless Dufour num-
ber [37] was defined as

$$Q = \frac{T \alpha^2}{c_p \beta^2} \left( \frac{\partial \mu}{\partial C} \right)_{P,T}, \hspace{1cm} (8)$$

where $\mu(P,T,C)$ is the chemical-potential difference per
unit mass [see Eq. (24) below] and $c_p$ is the isobaric specific
heat per unit mass. Note that $Q$ is a purely thermodynamic
quantity. The coupling strength of the Dufour effect de-
dpends on combinations of $Q$, $\mathcal{L}$, and $\Psi$ [see Eq. (10) below]. In
liquid mixtures, $\mathcal{L}$ is small and thus the Dufour effect is
gigligible [36,37]. On the other hand, in gas mixtures,
$\mathcal{L} = \mathcal{O}(1)$ and the Dufour effect may not necessarily be
ignored. When the effect is strong, it can significantly change
the bifurcation topology and the existence regimes of station-
ary and traveling-wave convection [37,38].

In order to understand the relevance of the Dufour effect
more quantitatively, we examine the various terms in the
governing equations [2,37,39] for RBC in binary mixtures.
Scaling lengths by $d$, time by $d^2/\kappa$, temperature by
$\kappa v/\alpha g d^3$, concentration by $\kappa v/\beta g d^3$, and $P/\rho$ by $\kappa^2/d^2$,
the Oberbeck-Boussinesq approximation leads to [37]

$$\frac{1}{\sigma} (\partial_t + \mathbf{v} \cdot \nabla) \mathbf{v} = - \nabla \Pi + (\theta + c) \mathbf{\hat{z}} + \nabla^2 \mathbf{v}, \hspace{1cm} (9)$$

$$(\partial_t + \mathbf{v} \cdot \nabla) \theta = R \mathbf{v} \cdot \mathbf{\hat{z}} + (1 + \mathcal{L} Q \Psi) \nabla^2 \theta - \mathcal{L} \mathcal{Q} \Psi \nabla^2 \mathbf{c}, \hspace{1cm} (10)$$

$$(\partial_t + \mathbf{v} \cdot \nabla) c = R \Psi \mathbf{v} \cdot \mathbf{\hat{z}} + \mathcal{L} \nabla^2 (c - \Psi \theta), \hspace{1cm} (11)$$
where \(\theta(x,y,z)\), \(c(x,y,z)\), and \(p(x,y,z)\) are the deviations of \(T\), \(C\), and \(P\) from their values in the conduction state. Here \(x\) and \(y\) are the horizontal axes, \(z\) is the vertical axis opposite the direction of gravity, and \(\mathbf{\hat{z}}\) is the unit vector along \(z\). The Dufour effect changes the temperature-field equation [Eq. (10)] both “diagonally” via \(\Delta Q \Psi \nabla^2 \theta\) and “off diagonally” via \(-\Delta Q \Psi \nabla^2 c\). Thus a significant Dufour effect should occur when the parameter combinations \(\Delta Q \Psi \) and/or \(\Delta Q \Psi \frac{\partial}{\partial z}\) are sufficiently large. Although Linz [40,41] and Hort et al. [37] roughly estimated the parameters for binary-gas mixtures, there has been no direct assessment of the Dufour effect for any real gas mixtures because a complete set of thermophysical properties is rarely documented. In this paper, we determine all the necessary properties for several binary-gas mixtures with good accuracy. It turns out that the role of the Dufour effect in all of these is very minor. The reason for this is that \(\Psi\) tends to be small when \(Q\) is large. We test the predictions of linear [37] and weakly nonlinear [38] theory based on the above equations by measuring the critical Rayleigh number \(R_c\), the critical wave number \(k_c\), and the Nusselt number \(N_c\) near onset.

One can see from Eqs. (9)–(11) that the Prandtl number \(\sigma\) determines the relative weight of the nonlinear terms \(\mathbf{v} \cdot \nabla \mathbf{v}\), \(\mathbf{v} \cdot \nabla \theta\), and \(\mathbf{v} \cdot \nabla c\). The stability and evolution of convection patterns depend greatly on which nonlinear terms are dominant. The term \(\mathbf{v} \cdot \nabla \mathbf{v}\) can yield a vertical-vorticity field [5,42] giving rise to large-scale horizontal flows, whose magnitude is inversely proportional to \(\sigma\). It has been shown theoretically [42–45] and experimentally [46,47] that the large-scale flows are responsible for much of the complex spatiotemporal behavior of convection patterns observed at low Prandtl numbers [5,12,16–18]. Thus it is of great interest to investigate the role of \(\sigma\) quantitatively, especially for \(\sigma \leq 1\). However, as a material property, \(\sigma\) cannot be readily adjusted in a given experiment. Prandtl numbers of pure gases generally are larger than the value 2/3 derived from kinetic theory for rigid-sphere molecules [48]. Liquid metals have \(\sigma \leq 0.03\), but we know of no classical pure fluids [49] with \(0.03 \leq \sigma \leq 0.67\). Employing simplified models, Giaocobbe [50] estimated the Prandtl number for binary noble-gas mixtures involving helium and found that \(\sigma\) can reach about 0.2 for a helium-xenon mixture. In the present paper, we use a more accurate method, based on a combination of statistical-mechanical theory and experimental data from the literature and our experiments, to show that \(\sigma\) as low as 0.16 can be achieved by a hydrogen-xenon mixture. In our experiments we cover the range 0.16 \(\leq \sigma \leq 1.00\) by using different binary-gas mixtures and pure gases and by changing their pressures and concentrations. Some results for the effect of the Prandtl number on spiral-defect chaos have been reported in Ref. [25] and we plan to present more detailed results in another paper [51].

The rest of this paper is organized as follows. In Sec. II we describe the general method used to obtain the thermophysical properties of pure gases and binary-gas mixtures required in the study of RBC. We also explain why Prandtl numbers can be lowered in binary-gas mixtures with a simple model. Section III presents the experimental setup and measurement methods. Experimental results for the onset of convection are presented in Sec. IV. Finally, in Sec. V we discuss the relative importance of the Soret and Dufour effects in binary-gas mixtures and give a summary of our work.

### II. THERMOPHYSICAL PROPERTIES OF BINARY-GAS MIXTURES

Under ideal circumstances the physical properties of gases and their mixtures would be based on experimental determinations. Unfortunately, the amount of experimental data required for our needs is formidable and we must resort to less satisfactory approaches. Whenever possible, we used experimental measurements. When these were inadequate, we employed theoretical estimates based on kinetic theory and empirical interpolation formulas. This approach does not lend itself to a systematic presentation because the details vary from case to case. Thus, in this section we attempt to present the general methods that we have used. The details will differ for different mixtures, and more specific information including references to the literature for each of them is presented in the Appendix.

To study RBC in gases quantitatively, we need to know the “primary” thermophysical properties listed in Table I. Other thermodynamic and transport coefficients derivable from them are the kinematic viscosity \(\nu = \eta/\rho\), the thermal diffusivity \(\kappa = \lambda/\rho c_p\), the thermal and solutal expansion coefficients given by Eqs. (2) and (6), and the specific heat per unit mass \(c_p = C_p/M\). Here

\[
M = M_2X + M_1(1-X)
\]  

is the molar mass of the mixture and \(M_1\) and \(M_2\) are the molar masses of the lighter and heavier pure component, respectively. The mole fraction \(X\) of the heavier component is given by

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**Table I.** Primary thermophysical properties of pure gases and binary-gas mixtures. The quantity \(X\) denotes the mole fraction of the heavier component in a mixture.

<table>
<thead>
<tr>
<th>Property</th>
<th>Pure gas</th>
<th>Binary-gas mixture</th>
</tr>
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<tbody>
<tr>
<td>density (\rho(P,T))</td>
<td>(\rho(P,T,X))</td>
<td></td>
</tr>
<tr>
<td>shear viscosity (\eta(P,T))</td>
<td>(\eta(P,T,X))</td>
<td></td>
</tr>
<tr>
<td>thermal conductivity (\lambda(P,T))</td>
<td>(\lambda(P,T,X))</td>
<td></td>
</tr>
<tr>
<td>isobaric specific heat (per mole) (C_p(P,T))</td>
<td>(C_p(P,T,X))</td>
<td></td>
</tr>
<tr>
<td>mass diffusivity (D(P,T))</td>
<td>(D(P,T,X))</td>
<td></td>
</tr>
<tr>
<td>thermal diffusion ratio (k_f(P,T))</td>
<td>(k_f(P,T,X))</td>
<td></td>
</tr>
<tr>
<td>chemical-potential difference (\mu(P,T))</td>
<td></td>
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</table>

*See Eq. (24) for the definition.*
\[ X = N_2 / (N_1 + N_2), \]  
(13)

where \( N_1 \) and \( N_2 \) are the number of moles of the lighter and heavier component, respectively. In the hydrodynamic equations the mass concentration often is used and it is given by

\[ C = N_2 M_2 / (N_1 M_1 + N_2 M_2). \]  
(14)

The relationship between \( X \) and \( C \) is easily derived to be

\[ C = X M_2 / M \]  
(15)

and the derivative \( dC/dX \) is given by

\[ dC/dX = M_1 M_2 (N_1 + N_2)^2 / (N_1 M_1 + N_2 M_2)^2. \]  
(16)

We wrote a series of programs to calculate the thermophysical properties of eight pure gases (He, Ne, Ar, Xe, \( H_2 \), \( N_2 \), \( CO_2 \), and \( SF_6 \)) and six binary-gas mixtures (He-Xe, He-CO\(_2\), He-SF\(_6\), Ne-Ar, Ar-CO\(_2\), and \( H_2\)-Xe) as a function of temperature and pressure. Using the same procedure, it is possible to determine thermophysical properties for many other binary-gas mixtures, especially noble-gas mixtures. The properties calculated in this work are applicable to the range 0°–60 °C and 1–50 bars, except that the partial pressure of temperature and pressure. Using the same procedure, it is possible to determine thermophysical properties for many other binary-gas mixtures, especially noble-gas mixtures. The properties calculated in this work are applicable to the range 0°–60 °C and 1–50 bars, except that the partial pressure of temperature and pressure. Using the same procedure, it is possible to determine thermophysical properties for many other binary-gas mixtures, especially noble-gas mixtures. The properties calculated in this work are applicable to the range 0°–60 °C and 1–50 bars, except that the partial pressure of

\[ B(T,X) = (1-X)^2 B_1(T) + 2X(1-X)B_{12}(T) + X^2 B_2(T), \]  
(18)

where \( B_1 \) and \( B_2 \) are the second virial coefficients of components 1 and 2, respectively, and \( B_{12} \) the second interaction virial coefficient associated with the unlike pair interaction between components 1 and 2. The coefficient \( B_{12}(T) \) has been measured for many mixtures [62–66] and can be calculated by statistical-mechanical theory for some of them [59,61]. The third virial coefficient is sometimes necessary to improve the accuracy of mixture densities, but the third unlike interaction virial coefficients are seldom available. So the third virial coefficients of pure gases were used to evaluate \( C(T,X) \) approximately.

2. Viscosity, thermal conductivity, and heat capacity

For both physical reasons and practical purposes, \( \eta(p,T,X) \) and \( \lambda(p,T,X) \) are expressed as a sum of two independent contributions [32,67]. Thus, writing \( Y(p,T,X) \) for both properties we have

\[ Y(p,T,X) = Y_0(T,X) + \Delta Y(p,T,X). \]  
(19)

Here \( Y_0(T,X) = Y(0,T,X) \) is the contribution to the transport property in the limit of zero density, where only two-body molecular interactions occur. The second term \( \Delta Y(p,T,X) \) represents the contribution of all other effects to the transport property at elevated densities, such as many-body collisions and collisional transfer. It can be expanded as a polynomial of \( p \).

\[ \Delta Y(p,T,X) = Y_1(T,X)p + Y_2(T,X)p^2 + Y_3(T,X)p^3 + \cdots. \]  
(20)

The expansion (20) is usually kept up to the second or third term. For the relatively narrow temperature range used in our experiment, \( Y_1(T,X) \) and \( Y_2(T,X) \), etc., are sometimes assumed to be temperature independent, depending on the data available to us. Similarly, the heat capacity \( C_p(p,T,X) \) can also be expressed as Eq. (19) [32], where the first term is then due to the molecule’s translational, rotational, and vibrational degrees of freedom and the second term stands for the contribution of all intermolecular interactions. For the pure gases used in our experiment, \( \eta \), \( \lambda \), and \( C_p \) are tabulated in the literature and easily can be fitted to Eqs. (19) and (20).

For the binary-gas mixtures, the calculation of \( \eta \) and \( \lambda \) is much more complicated. Different methods have to be chosen, depending on the available data and theoretical results. For the noble-gas mixtures Ne-Ar and He-Xe, the zero-density viscosity \( \eta_0 \) and the zero-density thermal conductivity \( \lambda_0 \) can be calculated from kinetic theory and empirical integrals given by Kestin et al. [59] with an accuracy of 1% or so. For the mixtures involving polyatomic molecules, although \( \eta_0 \) can be calculated from kinetic theory [61,68], the thermal conductivity cannot be treated well by kinetic theory due to the internal degrees of freedom and anisotropic pair potentials. When there are enough reliable experimental data, such as for He-CO\(_2\) and Ar-CO\(_2\), both \( \eta_0 \) and \( \lambda_0 \) were obtained by fitting to the data the empirical expression [56,69,70].
where \( Y_{01} \) and \( Y_{02} \) are the zero-density values of the pure components and \( A_{12} \) and \( A_{21} \) are adjustable parameters. In the case of \( \text{H}_2\text{-Xe} \) and \( \text{He-SF}_6 \), we did not find enough data to apply Eq. (21). Thus the kinetic-theory equations and empirical integrals documented in Ref. [61] were used to calculate \( \eta_0 \) for \( \text{He-SF}_6 \), while the equations and integrals based on the Lennard-Jones potential summarized in Ref. [68] had to be employed to determine \( \eta_0 \) for \( \text{H}_2\text{-Xe} \). An approximate method due to Monchick et al. [71,72], which was summarized later in Ref. [73], was used to estimate \( \lambda_0 \) for \( \text{H}_2\text{-Xe} \) and \( \text{He-SF}_6 \). This method relates the mixture thermal conductivity to the thermal conductivity of its components and other properties of the system such as the viscosity and diffusion constants, which can be predicted accurately by kinetic theory. To get a good estimation of \( \lambda_0 \), these properties were obtained from experimental data whenever possible. Because the method may have relatively large errors, the final result of \( \lambda \) was checked by our own measurements. We show later that the approximate method can predict \( \lambda \) quite accurately for \( \text{He-SF}_6 \), but gives a result slightly smaller than the measured one for \( \text{H}_2\text{-Xe} \). In order to obtain the pressure dependence of the mixture \( \eta \) and \( \lambda \), we fitted Eq. (20) to experimental data whenever possible. When no data are available, we added the contributions of the two pure components together, i.e., \( \Delta Y(p,T,X) = \Delta Y_1(p_1,T) + \Delta Y_2(p_2,T) \), where \( p_1 \) and \( p_2 \) are the densities of two components in the mixture and \( p_1 + p_2 = \rho \). Since the pressure dependence of \( \eta \) and \( \lambda \) is usually small in our pressure range, such an approximation should work well.

Because the specific heat of a gas is mainly contributed by the molecule’s translational, rotational, and vibrational degrees of freedom, we assumed the contribution of unlike interactions of components 1 and 2 to be negligible. Hence we calculated the mixture heat capacity by adding the contributions of the two components together [50,70]:

\[
C_p(P,T,X) = (1 - X)C_p(1,T) + XC_p(2,P_2,T),
\]

where \( P_1 \) and \( P_2 \) are the partial pressures of components 1 and 2, respectively.

### 3. Diffusion constant and thermal diffusion ratio

The mass diffusivity \( D \) and the zero-density thermal diffusion ratio \( k_{T0} \) are given by kinetic theory [32,59,61]. The theory predicts that the product \( PD \) is constant for dilute gases. Hence, in studying the pressure dependence of \( D \), the product \( PD \) should be studied. To first order, the pressure dependence of both \( PD \) and \( k_T \) can be written as [74–77]

\[
Z(P,T,X) = Z_0(P,T,X)[1 + B_{\eta}(X,T)P],
\]

where \( Z(P,T,X) \) stands for both \( PD \) and \( k_T \), and \( Z_0(P,T,X) \) for their zero-pressure values. The second “virial coefficient” \( B_{\eta}(X,T) \) is a function of concentration and temperature. Unfortunately, there are only limited data on the pressure dependence of \( k_T \) and \( PD \). We used the measurements of \( B_{\eta}(X,T) \) for \( \text{He-CO}_2 \) and \( \text{He-SF}_6 \) by Trengove et al. up to 5 atm [76] and employed approximate methods summarized in Refs. [74,75] and in Refs. [76,77] to calculate \( B_{\eta}(X,T) \) and \( B_{k_T}(X,T) \), respectively, from the second virial coefficients of pure gases and mixtures. Dunlop and his collaborators [74–76] have tested these methods experimentally for several mixtures at relatively low pressures (up to 5 atm for \( k_T \) and 9 atm for \( PD \)). However, the second virial coefficient \( B_{k_T}(X,T) \) may not be sufficient because of the strong pressure dependence of \( k_T \).

Finally, we point out that the value of \( k_T \) depends on which concentration one uses, the mole fraction \( X \) or the mass concentration \( C \). The original definition of \( k_T \) [34] is based on the mole fraction; however, the mass concentration is used in the governing equations and the separation ratio. The two values of \( k_T \) are converted from one to another by \( k_{T,\text{mass}} = (dC/dX)k_{T,\text{mole}} \), where \( (dC/dX) \) is given by Eq. (16).

### 4. Chemical potential

The chemical-potential difference per unit mass of the mixture \( \mu(P,T,C) \) is given by [39]

\[
\mu = \mu_2/M_2 - \mu_1/M_1,
\]

where \( \mu_1 \) and \( \mu_2 \) are the chemical potentials per mole of the single components. Assuming the mixtures are ideal gases [37], we have

![FIG. 1. Shear viscosity \( \eta \) as a function of the mole fraction \( X \) of the heavy component in binary mixtures. The symbols are experimental data and the curves are the results calculated from the fits used in this work at the corresponding \( P \) and \( T \). (a) The open circles [78] are for \( \text{H}_2\text{-Xe} \) at \( P = 1.0 \text{ bar and } T = 23 \text{ °C} \), the solid circle [53] is for pure Xe at the same condition, and the squares [79] are for \( \text{He-CO}_2 \) at \( P = 23.3 \text{ bars and } T = 30 \text{ °C} \). (b) The triangles [80] are for \( \text{He-SF}_6 \) at \( P = 1.0 \text{ bar and } T = 25 \text{ °C} \) and the diamonds [81] are for \( \text{He-CO}_2 \) at \( P = 1.0 \text{ bar and } T = 25 \text{ °C} \).](Image 339x467 to 537x736)
4–7% for $k_T$ molecules. Because of the strong pressure dependence of noble-gas mixtures than for mixtures involving polyatomic molecules. For the pure gases, the estimated accuracies are about 2% for $\rho$, $\eta$, $\lambda$, and $C_p$. For the six binary mixtures, the estimated accuracies are about 2% for $\rho$ and $\eta$, 2–5% for $\lambda$, 4–7% for $D$, and 5–10% for $k_T$. The accuracy is better for noble-gas mixtures than for mixtures involving polyatomic molecules. Because of the strong pressure dependence of $k_T$ and the lack of data at elevated pressures, the accuracy of $k_T$ is relatively poor. There are no experimental data for $C_p$, but we estimated that its accuracy is within 5% for the relatively low pressures used in this experiment.

In Figs. 1–3 we present several examples of the shear viscosity $\eta$, the thermal conductivity $\lambda$, and the reduced low-density thermal diffusion ratio $\alpha_{T0} = k_{T0,mole}/X(1-X)$ as functions of $X$. To compare with experimental data, the calculations were done at the pressures and temperatures of those experiments cited in the figures. The results agree with the experiments within the accuracies given above. It is interesting to note the agreement between our measured $\lambda$ and the calculated one for He-SF$_6$ in Fig. 2(a). The measurement method of $\lambda$ and more comparisons are given in Sec. III D.

**B. Dimensionless numbers**

Now we can calculate the four dimensionless material properties required in the study of RBC in binary-gas mixtures, namely, the separation ratio $\Psi$, the Lewis number $L$, the Dufour number $Q$, and the Prandtl number $\sigma$. In Figs. 4–7 these parameters are presented as functions of the mole fraction $X$ of the heavy component for $P=22$ bars and $T=25^\circ$C. The separation ratio $\Psi$ for all six mixtures is positive.

**FIG. 3.** Reduced low-density thermal-diffusion ratio $\alpha_{T0}$ as a function of the mole fraction $X$. The symbols are experimental data, and the curves are calculated from the fits used in this work at the corresponding $T$. Open [86] and solid [76] squares, He-SF$_6$ at $T=26.85^\circ$C; open [87] and solid [76] circles, He-CO$_2$ at $T=26.85^\circ$C; triangles [88], H$_2$-Xe at $T=26.85^\circ$C; diamonds [89], Ne-Ar at $T=21.85^\circ$C.

**FIG. 4.** Separation ratio $\Psi$ as a function of the mole fraction $X$ of the heavy component for $P=22$ bars and $T=25^\circ$C.
On the other hand, the separation ratio increases monotonically with the molar-mass ratio $M = M_2/M_1$ (Table II). If $M$ is close to one, the separation ratio is small, e.g., $\Psi_{\text{max}}$ is only $3.2 \times 10^{-3}$ for Ar-CO$_2$. However, when $M \approx 1$, the separation ratio can be quite large, as in the case of He-SF$_6$, where $\Psi_{\text{max}} = 0.85$. The peak position of $\Psi(X)$ shifts to low $X$ as $M$ increases. In the case of noble-gas mixtures, the separation ratio increases monotonically with $M$ at fixed $X$. Linz noted similar behavior in a previous analysis of Lorentz-gas mixtures [41]. This monotonic relation does not hold well for binary-gas mixtures involving polyatomic molecules (Fig. 4).

The Lewis numbers increase with $X$ from minimum values between 0.2 and 0.7 near $X = 0$ to maximum values between 1.6 and 22 near $X = 1$ (Fig. 5). The maximum value is 22 for He-SF$_6$ and 13.7 for H$_2$-Xe. On the other hand, the Dufour number is proportional to $1/C(1 - C)$ [Eq. (26)] and thus diverges in the pure-gas limits (Fig. 6). The minimum value of $Q(X)$ is about 34 for Ar-CO$_2$ and 3.2 for Ne-Ar, but $Q$ is close to zero for the other four mixtures with $M > 10$ except near the pure-gas limits (Fig. 6). More interestingly, for all mixtures except Ar-CO$_2$, the Prandtl number is lower than that of either pure component over most of the range of $X$ (Fig. 7). The minimum value of $\sigma$ decreases almost monotonically with increasing $M$ as shown in Table II.

One sees from Figs. 4 and 6 and Table II that $\Psi$ and $Q$ do not both have large values under the same conditions. Since the strength of the Dufour effect depends on $LQ\Psi$ and $LQ\Psi^2$ [Eq. (10)], we plotted these two parameter combinations vs $X$ for Ar-CO$_2$ and He-SF$_6$ in Fig. 8. The values of both $LQ\Psi$ and $LQ\Psi^2$ are so small for Ar-CO$_2$ that the Dufour effect is very weak even though $Q$ is large. For He-SF$_6$, the value of $LQ\Psi^2$ is small, but $LQ\Psi$ can be relatively large. Hence it is not straightforward to determine the strength of the Dufour effect for this mixture without additional analysis. Therefore, we discuss the influence of the Dufour effect on the onset of convection in detail in Sec. V A.

C. Why is the Prandtl number lowered in binary-gas mixtures?

It is worthwhile to understand why the Prandtl number is lowered in binary-gas mixtures. This may be useful also in design engineering involving heating or refrigeration systems [50,90], where reducing $\sigma$ may increase the heat-transfer coefficient. Kinetic theory for rigid-sphere molecules [48] predicts $\eta = a(MT)^{1/2}/\delta^2\Omega$ and $\lambda = b(T/M)^{1/2}/\delta^2\Omega$, where $a$ and $b$ are constants, $\delta$ is the molecular diameter, $\Lambda$ is the thermal diffusivity, and $\Omega$ is the specific heat. The Prandtl number is then $\sigma = \lambda/\eta = b/(aM)^{1/2}$.

### Table II

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$M$</th>
<th>$\sigma_{\text{min}}$</th>
<th>$\Psi$</th>
<th>$\mathcal{L}$</th>
<th>$Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar-CO$_2$</td>
<td>1.1</td>
<td>0.683</td>
<td>0.0032</td>
<td>1.085</td>
<td>37.82</td>
</tr>
<tr>
<td>Ne-Ar</td>
<td>2.0</td>
<td>0.628</td>
<td>0.035</td>
<td>0.912</td>
<td>3.519</td>
</tr>
<tr>
<td>He-CO$_2$</td>
<td>11.0</td>
<td>0.408</td>
<td>0.268</td>
<td>1.496</td>
<td>0.395</td>
</tr>
<tr>
<td>He-Xe</td>
<td>32.8</td>
<td>0.209</td>
<td>0.299</td>
<td>1.285</td>
<td>0.427</td>
</tr>
<tr>
<td>He-SF$_6$</td>
<td>36.5</td>
<td>0.300</td>
<td>0.470</td>
<td>2.565</td>
<td>0.166</td>
</tr>
<tr>
<td>H$_2$-Xe</td>
<td>65.1</td>
<td>0.168</td>
<td>0.232</td>
<td>1.238</td>
<td>0.357</td>
</tr>
</tbody>
</table>

![Figure 5](image5.png) **FIG. 5.** Lewis number $\mathcal{L}$ as a function of the mole fraction $X$ of the heavy component. Solid line, H$_2$-Xe; dashed line, He-CO$_2$; dot-dashed line, He-SF$_6$; dotted line, Ne-Ar. To improve the clarity of this figure, we do not plot the results for Ar-CO$_2$ and He-Xe, which are close to those of Ne-Ar and H$_2$-Xe, respectively. For these data $P = 22$ bars and $T = 25^\circ$C.

![Figure 6](image6.png) **FIG. 6.** Dufour number $Q$ as a function of the mole fraction $X$ of the heavy component. The curves that are not labeled are for H$_2$-Xe, He-Xe, He-CO$_2$, and He-SF$_6$ from top to bottom. The curves for H$_2$-Xe and He-Xe are nearly the same. For these data $P = 22$ bars and $T = 25^\circ$C.
Prandtl number is the heavy component. For these data \( P_{cp} \) also for binary noble-gas mixtures. The mixture heat capacity is and found

\[
\eta = \frac{(1-X)(M_1 T)^{1/2} + X(M_2 T)^{1/2}}{(1-X)\delta_1^2 \Omega_1 + X\delta_2^2 \Omega_2}
\] (28)

and

\[
\lambda = \frac{(1-X)(T/M_1)^{1/2} + X(T/M_2)^{1/2}}{(1-X)\delta_1^2 \Omega_1 + X\delta_2^2 \Omega_2}
\] (29)

for binary noble-gas mixtures. The mixture heat capacity is also \( c_p = (5/2)A/M \), with \( M \) given by Eq. (12). Then the Prandtl number is

\[
\sigma = \frac{2}{3} \left( \frac{1-X}{(1-X) + XM} \right)^{1/2}
\] (30)

FIG. 8. Coefficients of the Dufour effect in Eq. (10), \( LQ\Psi \) and \( LQ\Psi^2 \), for He-SF\(_6\) and Ar-CO\(_2\). Solid line, \( LQ\Psi^2 \) for He-SF\(_6\); dashed line, \( LQ\Psi \) for He-SF\(_6\); dot-dashed line, \( LQ\Psi^2 \) for Ar-CO\(_2\); dotted line, \( LQ\Psi \) for Ar-CO\(_2\). For these examples \( P = 22 \) bars and \( T = 25 \) °C.

FIG. 9. Ratio \( \eta/\lambda \) (dashed curve) and the heat capacity per unit mass \( c_p \) (solid curve) as a function of \( X \) for He-SF\(_6\). For this example \( P = 22 \) bars and \( T = 25 \) °C.

It can be shown analytically that the denominator in Eq. (30) is larger than the numerator for \( 0 < X < 1 \) if \( M > 1 \). The denominator equals the numerator for pure gases \( (X = 0,1) \). A larger value of \( M \) yields a smaller value of \( \sigma \) for a fixed \( X \). Therefore, the Prandtl number of binary-gas mixtures is always smaller than that of pure gases for a rigid-sphere model. The smallest value of \( \sigma \) decreases with increasing \( M \). This argument can be extended to binary-gas mixtures involving polyatomic molecules by employing the Eucken correction [48] in the estimate of the thermal conductivity of polyatomic gases. For two pure components \( \eta/\lambda \approx M \), so the ratio is small for the light component and large for the heavy one. Since the square roots of the molar masses enter into \( \eta/\lambda \), the ratio grows relatively slowly as \( X \) increases until \( X \) is close to one (see Fig. 9 for an example of a real gas mixture). However, in the mass heat capacity \( c_p \), the mass of the heavy molecule is more important and \( c_p \) drops quickly as \( X \) increases from 0 and then begins to level off (Fig. 9). Hence the product of \( \eta/\lambda \) and \( c_p \) reaches a minimum at a middle value of \( X \).

In Fig. 10 we compare the estimates based on the MFW approximation with our numerical results for \( P = 1 \) bar and \( T = 25 \) °C for four mixtures. In the case of a monatomic (noble) gas mixture, the MFW method predicts a minimum value of \( \sigma \) very close to the real value, but at a somewhat different concentration [Fig. 10(a)]. In the case of mixtures involving polyatomic gases [Fig. 10(b)], two MFW curves are shown for each mixture: the dashed curve assumes a polyatomic molecule to be a monatomic one having the same mass, while the dot-dashed curve takes the internal degrees of freedom into account when estimating the thermal conductivity and heat capacity. It is apparent that the internal degrees of freedom increase the minimum Prandtl number. The increase is more significant when a polyatomic molecule consists of a larger number of atoms. For example, the molar-mass ratio \( M \) of He-SF\(_6\) is larger than that of He-Xe, but its minimum \( \sigma \) is considerably higher than that of He-Xe (Fig. 7). Therefore, H\(_2\)-Xe is actually the binary-gas mixture giving the smallest \( \sigma \), since all mixtures with a larger \( M \) involve more internal degrees of freedom.

III. EXPERIMENTAL METHOD

A. Apparatus and gases

The apparatus was described in detail by de Bruyn et al. [8]. We used three convection cells with \( \Gamma = 30 \) (cell 1:...
Circular sidewalls made of porous filter paper. The plates:
- Top plate: a diamond-machined aluminum bottom plate, and the plates vary as the experimental control parameter. The gas-filled cell 2: cell 3: cell 1:
- Temperature and concentration fields horizontally, leading to spatial variation of the vertical average of the refractive index in the x-y plane, which is visualized by the shadowgraph method.

All gases were purchased from Air Liquide America Corporation. Their purity was better than 99.99%. We used three pure gases (Ar, CO₂, and SF₆) and four binary-gas mixtures (Ne-Ar, He-CO₂, He-SF₆, and H₂-Xe) in convection experiments. By choosing different mixtures and pure gases and by varying their concentration and pressure, we varied \( \sigma \) from 0.17 to 1.01, \( \Psi \) from 0 to 0.80, \( L \) from 0.67 to 6.35, and \( Q \) from 0.07 to 4.51 (see Tables IV and V below). Three other pure gases (He, Ne, and N₂) were used as well to calibrate the heat conduction of the cell walls.

The H₂-Xe mixture was purchased from the manufacturer who specified the mole fraction of xenon to be \( X = 49.6\% \) with an accuracy of better than \( \pm 1\% \). The Ne-Ar, He-CO₂, and He-SF₆ mixtures were prepared in our laboratory from the pure gases. Before filling the mixing cylinder, we flushed it with the first component several times. After the cylinder was filled with the first component, the pressure \( P \) and temperature \( T \) were measured. The concentration was then determined from the mixture's equation of state by finding the value \( X \) that gives the correct density of the first component. The pressures and temperatures were always measured after thermal and concentration equilibrium was reached. To minimize the error from uncertainties in the equation of state (which is largest at the highest pressures), the final mixture pressure was kept as low as possible and yet high enough to fill the convection cell to the desired pressure of the experiment. The concentration accuracy of our mixtures was \( \pm (1 - 2)\% \).

The onset of convection was determined by measuring the Nusselt number \( \mathcal{N} \) and the shadowgraph-image contrast. By definition, \( \mathcal{N} = 1 \) in the conduction state. As convection starts, \( \mathcal{N} \) increases with \( \Delta T \) because the heat transport is enhanced by convection. The convection modulates the temperature and concentration fields horizontally, leading to spatial variation of the vertical average of the refractive index in the x-y plane, which is visualized by the shadowgraph method.

B. Heat conduction of the cell wall

To measure the Nusselt number \( \mathcal{N} \) and the thermal conductivity of the gas mixtures precisely, we calibrated the heat conduction of the cell sidewall using six pure gases (He, Ne, Ar, N₂, CO₂, and SF₆) with a wide range of known thermal conductivities. In the conduction state, the conductance (equal to the heat current per unit temperature difference) of the gas inside the cell is \( Q = A \lambda / d \), where \( A = \pi r^2 \) is the cell area. The conductance \( Q_\text{w} \) of the sidewall, foam, solid supports, and the gas outside the cell can be modeled as heat...
TABLE III. Comparison of the thermal conductivities of binary-gas mixtures measured in this experiment (λ_m) with the ones calculated with our programs (λ_c).

<table>
<thead>
<tr>
<th>Mixture</th>
<th>T (°C)</th>
<th>P (bars)</th>
<th>X</th>
<th>100λ_m (W/mK)</th>
<th>100λ_c (W/mK)</th>
<th>100(λ_m−λ_c)/λ_c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne-Ar</td>
<td>23.0</td>
<td>36.65</td>
<td>0.680</td>
<td>2.584</td>
<td>2.560</td>
<td>0.9</td>
</tr>
<tr>
<td>He-CO₂</td>
<td>21.0</td>
<td>30.60</td>
<td>0.537</td>
<td>4.888</td>
<td>4.730</td>
<td>3.3</td>
</tr>
<tr>
<td>He-CO₂</td>
<td>22.5</td>
<td>25.97</td>
<td>0.879</td>
<td>2.457</td>
<td>2.459</td>
<td>-0.1</td>
</tr>
<tr>
<td>He-SF₆</td>
<td>20.5</td>
<td>28.10</td>
<td>0.199</td>
<td>7.476</td>
<td>7.539</td>
<td>-0.8</td>
</tr>
<tr>
<td>He-SF₆</td>
<td>25.0</td>
<td>18.79</td>
<td>0.578</td>
<td>3.156</td>
<td>3.162</td>
<td>-0.2</td>
</tr>
<tr>
<td>H₂-Xe</td>
<td>20.0</td>
<td>15.33</td>
<td>0.380</td>
<td>4.861</td>
<td>4.711</td>
<td>3.2</td>
</tr>
<tr>
<td>H₂-Xe</td>
<td>21.0</td>
<td>20.67</td>
<td>0.496</td>
<td>5.539</td>
<td>5.271</td>
<td>5.1</td>
</tr>
</tbody>
</table>

C. The mean concentration for ΔT>0

For ΔT>0, the mean concentration X_m in the cell was slightly smaller than the initial value X_0 at ΔT=0 because Ψ>0 and the mean temperature inside the cell was larger than that outside the cell. We obtained X_m by measuring \( dQ/dT_m = 2(dQ/dΔT) \) in the conduction state. One has

\[
\frac{dQ}{dT_m} = \frac{\partial Q}{\partial T_m} + \frac{\partial Q}{\partial X} \frac{dX}{dT_m},
\]

and

\[
\frac{dλ}{dT_m} = \left( \frac{\partial λ}{\partial T_m} \right)_X + \left( \frac{\partial λ}{\partial X} \right)_T \frac{dX}{dT_m}.
\]

FIG. 12. Heat-transport measurement for a He-CO₂ mixture at X=0.52 and P=30.6 bars (Γ=30). (a) The total thermal conductance Q(ΔT) for the whole range of ΔT in this experiment and (b) Q(ΔT) near the onset of convection. Two solid lines in (b) are the linear fits to the data below and above the onset of convection, respectively. Their intersection gives the critical temperature difference ΔT_c=6.01 °C.

transport in porous media [91]. Then the total heat conductance \( Q = Q_g + Q_w \) can be expressed as

\[
Q = \frac{Aλ}{d} + a_1λ + a_2 = \frac{1}{a_3λ + a_4},
\]

where \( a_1 \) to \( a_4 \) are positive and depend on the properties of the filter paper and foam, the geometry outside the cell, the thermal conductivity of solid supports, and so on. These fitting parameters are temperature dependent.

In the experiment, we kept the top-plate temperature \( T_t \) constant and increased the bottom-plate temperature \( T_b \). This protocol caused the mean temperature \( T_m = (T_t + T_b)/2 \) and thus the average thermophysical properties and \( Q \) to vary with \( ΔT = T_b - T_t \) [92]. Furthermore, as \( ΔT \) changed, the mean concentration \( X_m \) inside the convection cell varied slightly because of the diffusion that resulted from the difference of the mean temperatures inside and outside the cell. The concentration variation also changed the properties and \( Q \). In short, when \( ΔT \) went up, \( T_m \) increased, while \( X_m \) decreased slightly for \( Ψ>0 \). For our mixtures, both increasing \( T_m \) and decreasing \( X_m \) raised the thermal conductivity, so \( Q \) increased with \( ΔT \). In the conduction state, we have the linear relationship

\[
Q(T, ΔT) = Q_0(T_i) + Q'(T_i) ΔT
\]

for not very large \( ΔT \) and the thicker cells 1 (\( d = 1.460 \) mm) and 2 (\( d = 1.500 \) mm), as confirmed by the heat-transport measurement [see Fig. 12(a)]. The quantity \( Q'(T) \) turned out to be small. For the thin cell 3 (\( d = 0.608 \) mm), however, we found that the quadratic term \( Q''(T_i)(ΔT)^2 \) had to be included in Eq. (32). Here \( Q'' \) is negative and its absolute value is smaller than \( Q' \) by a factor of 20–100.

We calibrated the cell conduction at \( T = T_i \) by extrapolating \( Q(T_i, ΔT) \) to \( ΔT = 0 \). Figure 11 shows a calibration result for cell 1 at \( T = 21 °C \). The average deviation of the fitted curve [solid line, Eq. (31)] from the experimental data (circles) is about 0.4%. The cell contribution \( Q_g \) and the wall contribution \( Q_w \) are plotted as dashed and dot-dashed curves, respectively, in Fig. 11. We note that the cell wall conducts more than half of the heat. Similar results were obtained for the other cells.

FIG. 12. Heat-transport measurement for a He-CO₂ mixture at X=0.52 and P=30.6 bars (Γ=30). (a) The total thermal conductance Q(ΔT) for the whole range of ΔT in this experiment and (b) Q(ΔT) near the onset of convection. Two solid lines in (b) are the linear fits to the data below and above the onset of convection, respectively. Their intersection gives the critical temperature difference ΔT_c=6.01 °C.
where \( \lambda = \lambda(T_m) \) is the mean thermal conductivity. The value of \( \partial Q/\partial \lambda \) was calculated from Eq. (31), while \((\partial Q/\partial T_m)_X\) and \((\partial Q/\partial X)_T\) were evaluated from the thermal conductivity of the gas mixture. The quantity \((\partial Q/\partial T_m)_X\) is due to the temperature dependences of \( a_1 \) to \( a_4 \) in Eq. (31) and was determined in the calibration of the cell conduction. Assuming all quantities in Eqs. (33) and (34) to be constant, we get \( dX/dT_m \) from Eqs. (33) and (34) and thus \( X_m = X_0 + (dX/dT_m) \Delta T/2 \). For \( \Psi > 0 \), \( dX/dT_m < 0 \).

D. Measurement of the thermal conductivity of the gas mixtures

The thermal conductivity \( \lambda \) of a gas mixture is determined from Eq. (31) by measuring \( Q \) with the gas mixture in the cell. The measured thermal conductivities \( \lambda_m \) and the calculated ones \( \lambda_c \) are given in Table III. The deviation \( (\lambda_m - \lambda_c)/\lambda_c \) listed in the table results from the errors of the thermal conductivity measurement and the determination of the concentration. The latter affects \( \lambda_c \).

The values of \( \lambda_m \) and \( \lambda_c \) agree well for Ne-Ar and He-CO\(_2\) at \( X = 0.879 \). The deviation of 3.3% for He-CO\(_2\) at \( X = 0.537 \) may be largely due to the concentration error since we know that the accuracy of \( \lambda_c \) is within 2% for He-CO\(_2\) mixtures by comparing \( \lambda_c \) with independent experimental data in the literature (see the Appendix). If, for instance, \( X = 0.527 \), then \( \lambda_c = 4.818 \times 10^{-2} \) W/mK, which is only 1.4% smaller than \( \lambda_m \). For three He-SF\(_6\) mixtures, the agreement is reasonably good, indicating that the approximate method due to Monchick et al. [71–73] is fairly accurate for this mixture. However, \( \lambda_m \) is more than 4% larger than \( \lambda_c \) for H\(_2\)-Xe. This deviation can only be partially attributed to a concentration error since the concentration accuracy given by the manufacturer is \( \pm 1 \% \). The difference may be largely due to the approximate nature of the method and the errors of the force constants for the Lennard-Jones potential [68]. In the remainder of this paper, we shall use \( \lambda_m \) for the H\(_2\)-Xe mixture and \( \lambda_c \) for the other five mixtures.

IV. EXPERIMENTAL RESULTS

A. Onset of convection

We determined the onset of convection for each gas or mixture by measuring the heat transport and the shadow-graph contrast. A typical example of heat-transport measurements is given in Fig. 12 for a run with a He-CO\(_2\) mixture having an initial concentration \( X = 0.537 \) (\( P = 30.60 \) bars, run 7 in Tables IV and V). The top-plate temperature was fixed at \( T_t = 21.0 \) °C, while the bottom-plate temperature \( T_b \) was increased in small steps from 21.0 °C to 33.5 °C. We allowed 2–6 h (over \( 2T^2\) \( t_r \), where \( t_r \) is the vertical thermal diffusion time) at each \( \Delta T \) for transients to decay before taking a time average of the total power \( p \) supplied to the bottom plate. Figure 12(a) gives the conductance \( Q = p/\Delta T \) versus \( \Delta T \) for this run. When \( \Delta T \) went up from zero, \( Q \) increased slowly and linearly in the conduction state. This increase is attributable primarily to the change in the mean concentration discussed in Sec. III C and to a lesser extent to the temperature dependence of gas conductivity and the wall conduction. At \( \Delta T = 6.0 \) °C, \( Q \) started to grow faster, showing that convection occurred. An enlarged view of \( Q(\Delta T) \) near the onset of convection is given in Fig. 12(b). To find the critical temperature difference \( \Delta T_c \) precisely, we fitted straight lines to the data below and above onset in Fig.
TABLE V. Dimensionless parameters and derived results for the experimental runs summarized in Table IV. See the text for notations.

<table>
<thead>
<tr>
<th>Run</th>
<th>$\sigma$</th>
<th>$\mathcal{L}$</th>
<th>$\Psi$</th>
<th>$Q$</th>
<th>$r_c^e$</th>
<th>$r_c^l$</th>
<th>$k_c^e$</th>
<th>$k_c^l$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.17</td>
<td>1.13</td>
<td>0.23</td>
<td>0.34</td>
<td>0.61</td>
<td>0.63</td>
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<td>2.9</td>
</tr>
<tr>
<td>2</td>
<td>0.18</td>
<td>1.19</td>
<td>0.29</td>
<td>0.34</td>
<td>0.54</td>
<td>0.58</td>
<td>2.8</td>
<td>2.9</td>
</tr>
<tr>
<td>3</td>
<td>0.30</td>
<td>0.67</td>
<td>0.80</td>
<td>0.07</td>
<td>0.23</td>
<td>0.25</td>
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<td>4</td>
<td>0.33</td>
<td>1.52</td>
<td>0.52</td>
<td>0.12</td>
<td>0.45</td>
<td>0.47</td>
<td>2.7</td>
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When there is no horizontal refractive-index variation, $I(x, \Delta T) = 0$ if we neglect experimental noise. When convection occurs, the refractive index is modulated horizontally, and for small modulation $I(x, \Delta T) \approx \delta n(x, \Delta T)$ [8, 31], where $\delta n(x, \Delta T)$ is the vertical average of the deviation of the refractive index from its mean value. Figure 13 shows the spatial average $\langle I^2(x, \Delta T) \rangle_s$ of the square of the shadowgraph signal as a function of $\Delta T$ near the ones of convection for the experiment described in Fig. 12. For $\Delta T < \Delta T_c$, the small positive constant value of $\langle I^2 \rangle_s$ (horizontal line in Fig. 13) is attributable to experimental noise. When $\Delta T > \Delta T_c$, there is an initially linear increase of $\langle I^2 \rangle_s$ with $\Delta T$ as shown in Fig. 13. The critical temperature difference determined by the shadowgraph method is $\Delta T_c = 6.01 \, ^\circ C \pm 0.01 \, ^\circ C$. The two methods giving the same $\Delta T_c$ demonstrates that the heat transport is enhanced significantly as soon as convection starts in binary-gas mixtures, similar to the case of pure fluids. In contrast, for binary-liquid mixtures with $\Psi > 0$, the heat conduction is enhanced so little for $\Delta T_c < \Delta T < \Delta T_{c0}$ that $\Delta T_c$ cannot be determined by heat-transport measurements [30, 31].

The convection patterns appearing at onset were rolls when $\Delta T_c$ was relatively small. Because of sidewall forcing [10, 11], as $\Delta T$ increased from below to above $\Delta T_c$, a concentric-roll (target) pattern appeared first [Fig. 14(a)]. It became unstable as

$$\epsilon = \frac{\Delta T - \Delta T_c}{1}.$$ 

FIG. 13. Determination of $\Delta T_c$ by the shadowgraph method for the experiment in Fig. 12: $(P^2)_s$ as a function of $\Delta T$. The data below $\Delta T_c$ are fitted to a horizontal line, while the data above $\Delta T_c$ are fitted to an inclined line. The intersection of the two lines gives $\Delta T_c = 6.01 \, ^\circ C$.

The critical wave number $k_c$ of the rolls at onset was calculated by Fourier analysis of the shadowgraph images. The dimensionless wave number is defined as $k = 2 \pi d / \lambda_w$, where $\lambda_w$ is the roll wavelength. We found $k_c < k_{c0} = 3.17$ for convection in binary-gas mixtures (Table V), where $k_{c0}$ is the critical wave number for convection in single-component fluids.

We calculated the critical Rayleigh number $R_c$ and the critical wave number $k_c$ based on the linear stability analysis

12(b). Their intersection gives $\Delta T_c = 6.01 \, ^\circ C \pm 0.01 \, ^\circ C$. Results for $\Delta T_c$ obtained by this method are summarized in Table IV. There we also list the mean concentration $X_{mc}$ and the mean temperature $T_{mc}$ at onset. Experiments with pure gases are given in the table for comparison.

In the shadowgraph method [8, 31], the initial (incoming) light intensity is $I_0(x)$, where $x$ is the horizontal position vector within the cell. The shadowgraph image at $\Delta T$ is denoted as $I(x, \Delta T)$. We define the shadowgraph signal as

$$I(x, \Delta T) = \frac{I(x, \Delta T)}{I_0(x)} - 1.$$ 

When there is no horizontal refractive-index variation, $I(x, \Delta T) = 0$ if we neglect experimental noise. When convection occurs, the refractive index is modulated horizontally, and for small modulation $I(x, \Delta T) \approx \delta n(x, \Delta T)$ [8, 31], where $\delta n(x, \Delta T)$ is the vertical average of the deviation of the refractive index from its mean value. Figure 13 shows the spatial average $\langle I^2(x, \Delta T) \rangle_s$ of the square of the shadowgraph signal as a function of $\Delta T$ near the ones of convection for the experiment described in Fig. 12. For $\Delta T < \Delta T_c$, the small positive constant value of $\langle I^2 \rangle_s$ (horizontal line in Fig. 13) is attributable to experimental noise. When $\Delta T > \Delta T_c$, there is an initially linear increase of $\langle I^2 \rangle_s$ with $\Delta T$ as shown in Fig. 13. The critical temperature difference determined by the shadowgraph method is $\Delta T_c = 6.01 \, ^\circ C \pm 0.01 \, ^\circ C$. The two methods giving the same $\Delta T_c$ demonstrates that the heat transport is enhanced significantly as soon as convection starts in binary-gas mixtures, similar to the case of pure fluids. In contrast, for binary-liquid mixtures with $\Psi > 0$, the

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of Hort, Linz, and Lücke [37] in order to compare the theory with our experiment, using a computer program provided by Hort and Lücke. The stability analysis takes both the Soret and Dufour effects into account. The calculations were done for the thermophysical properties at the mean temperature \(T_{mc} = T_1 + \Delta T/2\) and the mean concentration \(X_{mc}\) at the onset of convection.

In Table V we list the experimental results \(r_c^e\) and \(k_c^e\) for \(r_c = R_c / R_{c0} = \Delta T_c / \Delta T_{c0}\) and \(k_c\) for several mixtures, as well as the corresponding theoretical predictions \(r_c^t\) and \(k_c^t\). The mean temperature \(T_{mc}\) and the mean concentration \(X_{mc}\) at onset were listed already in Table IV. In addition, we give

FIG. 15. Nusselt number as a function of \(\epsilon\) for the experiment in Fig. 12.

the dimensionless numbers \(\sigma\), \(\Psi\), \(L\), and \(Q\) corresponding to these runs. The good agreement between experiment and theory for \(r_c^e\) and \(k_c^e\) shows that (i) the thermophysical properties are determined quite accurately and (ii) the evaluation of the linear stability analysis [37] is quite accurate. For most mixtures, \(r_c^e\) is a little smaller than \(r_c^t\). This is probably due to the underestimation of the thermal diffusion ratio \(k_T\) and thus of \(\Psi\) at elevated pressures by considering only the second virial coefficient for \(k_T\) [Eq. (23)] (the thermal diffusion ratio depends strongly on pressure). This idea is consistent with the result for the two \(\text{H}_2\)-Xe mixtures (Table V); the run at the larger pressure has a larger relative difference between \(r_c^e\) and \(r_c^t\).

**B. The Nusselt number**

We obtained the Nusselt numbers \(\mathcal{N}\) from the conductance \(Q_g = Q_w + Q_w\) of the gas inside the cell. It is given by

\[
\mathcal{N} = \frac{Q_g(\Delta T)}{Q_{g, cond}(\Delta T)} = \frac{Q(\Delta T) - Q_w(\Delta T)}{Q_{g, cond}(\Delta T)},
\]

where the heat conductance of the gas in the absence of convection

\[
Q_{g, cond}(\Delta T) = \frac{A}{d} \lambda(T_c) + 0.5 \lambda \left( \frac{dT}{dT} \right)
\]

and the sidewall contribution

\[
Q_w(\Delta T) = Q(T_c, \Delta T) - Q_{g, cond}(\Delta T)
\]

were determined from the heat-transport measurements in the conduction state [Eq. (32)] and the calibration of the sidewall conduction [Eq. (31)]. Their \(\Delta T\) dependence was extrapolated to the convection state. Figure 15 shows \(\mathcal{N}(\epsilon)\) for the measurements of \(Q(\Delta T)\) described in Fig. 12. In the conduction state \((\epsilon < 0)\) \(\mathcal{N} = 1\), while \(\mathcal{N} > 1\) in the convection state.

Near the onset of convection, \(\mathcal{N}\) can be expanded as

\[
\mathcal{N} = 1 + S_1 \epsilon + S_2 \epsilon^2 + \cdots,
\]

where \(S_1\) and \(S_2\) depend on \(\sigma\), \(\Psi\), \(Q\), and \(L\). The coefficient \(S_1\) is the initial slope of \(\mathcal{N}(\epsilon)\) at onset and is given by
The coefficient $S_2$ determines how $dN/d\epsilon$ changes with $\epsilon$ near onset. We determined the slope $S_1^c$ and $S_1^e$ by a straight-line extrapolation at small $\epsilon$ of the experimental data for $(N-1)/\epsilon$ from $\epsilon > 0$ to $\epsilon = 0$. The results $S_1^c$ and $S_1^e$ for several runs are given in Table IV. The value of $S_1^e$ is significantly larger than zero, in contrast to $S_1 \approx O(10^{-2})$ for convection in binary-liquid mixtures [30,31]. The quantity $S_2^c$ is always negative, indicating that $N$ increases more slowly as $\epsilon$ increases.

For pure fluids ($\Psi = 0$), the theoretical value $S_1^c(\sigma)$ for an infinitely extended pattern of perfect straight rolls was calculated exactly by Schlüter, Lortz, and Busse [94]. Although $S_1$ vanishes as $\sigma$ goes to zero, the dependence on $\sigma$ is weak for $\sigma \approx 0.35$ and $S_1^c(\sigma) = 1.42$ for $\sigma = 1$. Such a calculation is not available for the mixtures ($\Psi > 0$). However, employing a low-order Galerkin approximation for nonslip, impermeable boundary conditions at the top and bottom of the cell, Hollinger and Lücke [38] derived an eight-mode Lorenz model that pertains when stationary straight rolls are stable close to onset. We evaluated the initial slope $S_1^{HL}$ of $N$ from this model for the parameters of our experimental runs. However, due to the approximate nature of the model [38,95,96], it gives $S_1^{HL} = 1.718$ independent of $\sigma$ in the pure-fluid limit rather than the exact value 1.422 for $\sigma$ near one. Thus we made the empirical but reasonable estimate $S_1^e = (1.422/1.718)S_1^{HL}$. These values are compared with $S_1^e$ in Table IV. They are found to be systematically higher than $S_1^c$ by $0.2 - 0.3$. This difference between experiment and theory has long been known for pure fluids [97]. Presumably it is attributable to the depression of the heat transport in the experimental system by the boundaries, by roll curvature, and by defects in the pattern. We conclude that at best the difference $S_1^e(\Psi = 0) - S_1^e(\Psi)$ can be compared effectively with the corresponding theoretical prediction. Table IV suggests that the agreement for this difference is quite good.

FIG. 16. Initial slope of the Nusselt number at onset. (a) $S_1^e$ as a function of $\Psi$ and (b) $S_1^e$ as a function of $\delta S^f$ [see Eq. (43)] on log-log scale. The experimental (theoretical) values are given by solid (open) circles.

$$S_1^e(\Psi, \mathcal{L}) = \frac{2[1 + \Psi(1 + \mathcal{L}^{-2})]}{1 + \Psi(1 + \mathcal{L}^{-2} + \mathcal{L}^{-3})}. \tag{42}$$

However, for pure fluids, $S_1^e(\Psi = 0) = 2$, which is larger than the result of Schlier et al. for realistic rigid boundaries. Thus we examine only the difference $S_1^e(0) - S_1^e(\Psi, \mathcal{L})$ as a function of the scaling variable

$$\delta S^f = 2 - S_1^e(\Psi, \mathcal{L}). \tag{43}$$

This is done in Fig. 16(b), where we used the average experimental value $S_1^e(0) = 1.14$ from the three pure gases and

FIG. 17. Value of $S_1^e$ ($S_1^c$) as a function of $S_1^e$ ($S_1^c$). The experimental (theoretical) values are given by solid (open) circles.
the prediction \(S'_2(0) = 1.42\) of Schlüter et al. Both theory and experiment, to a very good approximation, fall on a single curve.

The theoretical value of \(S_2\) was also estimated by using the eight-mode model for both pure gases and binary-gas mixtures. The correction factor discussed above was employed, so \(S'_2 = (1.422/1.718)S_2\). The value of \(S'_2\) is listed in Table IV for some experimental runs. In Fig. 17, \(S'_2\) and \(S'_3\) are plotted as a function of \(S'_1\) and \(S'_4\), respectively. We find that \(S'_2\) agrees with \(S'_3\), though both of them are quite scattered and a smooth curve does not seem to exist. There is a clear trend that \(S_2\) decreases with increasing \(S_1\), i.e., as \(\varepsilon\) increases \(dN/d\varepsilon\) decreases more slowly for smaller initial slope \(S_1 = (dN/d\varepsilon)_{\varepsilon=0+}\).

**V. DISCUSSION**

**A. The strength of the Dufour effect**

The influence of the Dufour effect \((Q>0)\) depends on \(LQ\Psi\) and \(LQ\Psi^2\) [see Eq. (10)]. In Sec. II B we found that the values of these parameter combinations are small, for instance, for \(Ar-CO_2\) \((P=22\) bars, \(T=25^\circ C\)) even though \(Q\) itself is not small (Fig. 6). For \(He-SF_6\) under the same conditions, \(LQ\Psi^2\) is also small, but \(LQ\Psi\) can be relatively large (Fig. 8). Thus we examine the linear properties of this mixture, using stability analysis [37]. In Fig. 18 we plot \(r_c\) and \(k_c\) for the \(He-SF_6\) mixture with \((Q>0,\) solid line) and without \((Q=0,\) dashed line) the Dufour effect. The value of \(r_c\) increases very slightly when the Dufour effect is turned off, while \(k_c\) decreases by a small amount. The effect is at most of the same size as typical experimental errors and much smaller than the Soret effect. The other four mixtures (\(Ne-Ar, He-CO_2, He-Xe,\) and \(H_2-Xe\)) show a similar or weaker Dufour effect.

**B. Summary**

In this paper we presented the results of an extensive experimental investigation of Rayleigh-Bénard convection in binary-gas mixtures. A complete set of thermodynamic and transport properties was accurately determined for six binary-gas mixtures (\(He-CO_2, He-SF_6, He-Xe, Ne-Ar,\) \(Ar-CO_2,\) and \(H_2-Xe\)) by a combination of fitting data in the literature, doing molecular-theory calculations, and measuring the thermal conductivity ourselves. All six mixtures have positive separation ratios \(\Psi>0\) (Fig. 4). The Lewis number \(L\) is of order one (Fig. 5). An important feature of binary-gas mixtures is that their Prandtl number can be lower than that of the two pure components (Fig. 7). We discussed the physical reason and showed that the minimum Prandtl number that can be reached is about 0.16. Such low Prandtl numbers may be of technological importance in design engineering involving heating or refrigeration systems [50,90].

Both the heat-transport (Nusselt number \(N\)) measurements and the shadowgraph imaging gave the same critical temperature difference \(\Delta T_c\) for the onset of convection in binary-gas mixtures. The measured \(r_c=R_c/R_{c0}\) and \(k_c\) (Table V) agree well with the prediction of linear stability analysis [37]. In contrast to convection in binary-liquid mixtures having \(\Psi>0\), \(N\) increases significantly in binary-gas mixtures as soon as \(R_c\) is exceeded and convection starts. Consistent with predictions [35] for this parameter range, the convection patterns appearing near onset (Fig. 14) are rolls (hexagons appear at onset for relatively large \(\Delta T_c\)). So the convection in binary-gas mixtures behaves qualitatively like that in pure fluids, except that \(R_c<R_{c0}=1708\) and \(k_c<k_{c0}=3.117\). The initial slope of the Nusselt number \((dN/d\varepsilon)_{\varepsilon=0+}\) at onset was compared with that predicted by an eight-mode Galerkin truncation [38,96]. Good agreement was found for the variation of this slope with \(\Psi\) and \(L\) (Fig. 16). Based on the gas-mixture properties determined in this paper, we found that the Dufour effect (the reciprocal process of the Soret effect) is very weak in binary-gas convection (Fig. 18).

In view of the great variety of nonlinear phenomena found in binary-liquid mixtures with \(\Psi<0\) [29], it would be interesting to study RBC in binary-gas mixtures with negative separation ratios. Gas mixtures can have lower Prandtl numbers, larger Lewis numbers, larger aspect ratios, and faster time scales than liquid mixtures. Unfortunately, it appears that the separation ratio is always positive for relatively low pressures. A negative \(\Psi\) can perhaps be found in the critical region [99] and in very dense gases [100]. However, it is hard to obtain a complete set of thermophysical properties under those conditions.

Although so far binary-gas mixtures have been limited to \(\Psi>0\), they provide unique opportunities for the exploration of various nonlinear phenomena in RBC at Prandtl numbers between 0.16 and 1 and for Lewis numbers of order one. An important example is high-Rayleigh-number turbulent convection [7], where the nature of the boundary layers should
change as $\Psi$, $\sigma$, and $L$ are varied. Another is the quantitative study of the effect of $\sigma$ and $L$ on various secondary instabilities and spatiotemporal chaos. Using gas mixtures, we found recently that the onset of spiral-defect chaos depends significantly on the Prandtl number [25]. A detailed study of complex spatiotemporal behavior of convection patterns will be presented in another paper of this series [51].

ACKNOWLEDGMENTS

We wish to thank David S. Cannell for helpful discussions and St. Hollinger and M. Lücke for useful communications. W. Hort and M. Lücke kindly provided the program for the linear stability analysis. We are grateful to Greg Swift for alerting us to the opportunity to reach small $\sigma$ values in gas mixtures. This work was supported by the U.S. Department of Energy through Grant No. DE-FG03-87ER13738.

APPENDIX

Here we give major references for each gas and mixture. The actual methods used to obtain the thermophysical properties are briefly described. Since a large number of theoretical and fitting equations are involved, we do not reproduce them here.

1. Pure gases

a. $CO_2$

A precise high-order expansion for the equation of state is given by Vukalovich and Altunin [55]. Fits of suitable equations to data for $\eta$ and $\lambda$ are summarized by de Bruyn et al. [8]. The specific heat $C_p$ is tabulated in Ref. [55].

b. He

The equation of state is given by Tsederberg et al. [52] up to the third virial coefficient. These authors also give $C_p$ and fits to $\eta$ and $\lambda$. Some of their fits were cross-checked by experimental data from Ref. [101].

c. Ne and Ar

The second virial-coefficient $B$, zero-density $\eta$, and zero-density $\lambda$ were calculated from kinetic theory [59]. The density dependences of $\eta$ and $\lambda$ were obtained from fits to the data in Ref. [53]. The heat capacity $C_j$ is based on the data in Ref. [53]. We cross-checked the various estimates using the experimental data in Refs. [102,103].

d. Xe

All fits for $B$, $\eta$, $\lambda$, and $C_p$ are based on the data in Ref. [53]. Some of the fitting equations are given in that book. We cross-checked some results using the experimental data from Ref. [103].

e. $N_2$

Our estimate of the second virial-coefficient $B$ is based on a fit to the data in Ref. [60]. The estimates of the zero-density $\eta$ and $\lambda$ are fits to the data in Ref. [60] and in Ref. [104], respectively. Their density dependence was obtained from a fit to the data in Ref. [105] and in Ref. [106], respectively. For the heat capacity $C_p$ we used a fit to the data in Ref. [54].

f. $H_2$ (normal hydrogen)

The second virial-coefficient $B$ was obtained from a fit to the data in Refs. [63,107]. The zero-density $\eta$ and $\lambda$ are from fits to the data in Ref. [83]. The density dependence of $\eta$ is from a fit to the data of Ref. [105], while the density dependence of $\lambda$ is from Ref. [108]. The heat capacity $C_p$ is a fit to the data from Ref. [54].

g. SF$_6$

The equation of state is given in Ref. [109] up to the eighth virial coefficient. Equations for the thermal conductivity $\lambda$ are given in Ref. [110] and the equations for $\eta$ are given in Ref. [111]. The heat capacity $C_p$ at atmospheric pressure is a fit to the data in Ref. [104] and its pressure dependence is a fit to the data in Ref. [112].

2. Binary-gas mixtures

a. Ne-Ar

The second virial coefficient $B$ and zero-density $\eta$, $\lambda$, $D$, and $k_T$ were calculated from statistical-mechanical theory [59]. We took the density dependence of $\eta$ from that of the two pure components [53], while the density dependence of $\lambda$ was obtained by fitting to the data in Refs. [53,85]. No data are available for the pressure dependence of $D$ and $k_T$, so the models discussed in Sec. II A3 were used to estimate their pressure dependence. We cross-checked some of the results using the data in Refs. [81,85,89,102].

b. He-Xe

The second virial coefficient $B$ and zero-density $\eta$, $\lambda$, $D$, and $k_T$ were calculated by statistical-mechanical theory [59]. The density dependence of $\eta$ and $\lambda$ was obtained from the two pure components [53,103]. No data are available for the pressure dependence of $D$ and $k_T$, so the models discussed in Sec. II A3 were used to estimate their pressure dependence. Some of these results were cross-checked by the data in Refs. [78,113–115].

c. He-CO$_2$

An equation of state containing up to the fifth virial coefficient was used. The second virial coefficient $B$ was fitted to the data in Refs. [64,116]. The third virial coefficient $C$ was fitted to the data at $0^\circ$C [116] using the formula $C = C_{he}X_{he}^a + C_{co}X_{co}^a$. Here $a$ is the fitting parameter. The fourth and fifth virial coefficients were estimated from that of pure CO$_2$ neglecting helium, i.e., $D = D_{co}X_{co}^4$ and $E = E_{co}X_{co}^5$. For the zero-density $\eta$ and $\lambda$, Eq. (21) was fitted to the experimental data in Refs. [79,84]. Their density dependence was obtained from a fit to the data in Refs. [79,84]. The zero-density $D$ and $k_T$ were calculated from kinetic theory [61]. The pressure dependence of $k_T$ is given in Ref. [76] up to 5 atm, while the pressure dependence of $D$ was estimated
from the model discussed in Sec. II A3. The results for $D$ and $k_T$ were cross-checked by the data in Refs. [76,87,117–119].

d. $Ar-CO_2$

An equation of state containing terms up to the fifth virial coefficient was used. The second virial coefficient $B$ was fitted to the experimental data in Ref. [66]. The third coefficient was based on pure Ar [120] and CO$_2$ [55]. The fourth and fifth coefficients were based on those of pure CO$_2$ alone. We fitted Eq. (21) for the zero-density $\eta$ and $\lambda$ to the experimental data in Refs. [121,122] and in Ref. [84], respectively. The pressure dependence of $\eta$ was taken from that of the pure components, while the pressure dependence of $\lambda$ was fitted to the data from Ref. [84]. The zero-density $D$ and $k_T$ were calculated by kinetic theory [61]. The zero-density $D$ and $k_T$ were also calculated from kinetic theory [61]. However, we corrected $k_T$ based on the experimental data in Refs. [76,86,87] since the calculated values were systematically smaller than the experimental data. The pressure dependence of $D$ is given up to 9 atm at 300 K by Ref. [75], while the pressure dependence of $k_T$ is given by Ref. [76] up to 5 atm.

e. $He-SF_6$

We used an equation of state containing terms up to the fourth virial coefficient. The second virial coefficient $B$ was calculated from kinetic theory except that $B_{12}$ was corrected using the data from Refs. [64,65]. The third virial coefficient was based on the two pure components, while the fourth virial coefficient was estimated from pure SF$_6$. The zero-density $\eta$ was calculated from kinetic theory [61], while the zero-density $\lambda$ was estimated by the approximate method due to Monchick et al. (see Sec. II A2). The pressure dependence of $\eta$ and $\lambda$ was taken from that of the two pure gases. The zero-density $D$ and $k_T$ were also calculated from kinetic theory [61]. However, we corrected $k_T$ based on the experimental data in Refs. [76,86,87] since the calculated values were systematically smaller than the experimental data. The pressure dependence of $D$ is given up to 9 atm at 300 K by Ref. [75], while the pressure dependence of $k_T$ is given by Ref. [76] up to 5 atm.

f. $H_2-Xe$

The second virial coefficient was determined from Refs. [53,63,107]. The zero-density $\eta$ was calculated from kinetic theory based on a Lennard-Jones potential [68]. The zero-density $\lambda$ was estimated by the method of Monchick et al. The density dependence of $\eta$ and $\lambda$ was based on that of the pure gases. The zero-density $D$ and $k_T$ were calculated from kinetic theory [68]. Their density dependence was estimated from the models discussed in Sec. II A3. Some theoretical results were cross-checked by the data in Refs. [78,82,88,123].


[33] Thermal diffusion is the mass diffusion induced by a temperature gradient, while the ordinary mass diffusion results from concentration gradients. However, the term “thermal diffusion time” denotes the characteristic time of temperature relaxation due to thermal conduction.

[34] See p. 519 of Ref. [32].


[48] See pp. 16 and 527 of Ref. [32].

[49] An exception is liquid helium. As the superfluid-transition temperature 2.17 K is approached from above, σ vanishes. However, experiments are difficult because σ varies from a value of order one to zero over a narrow temperature range of a few mK and because of the problem of flow visualization, which has only recently been achieved under the required cryogenic conditions [A. L. Woodcraft, P. G. J. Lucas, R. G. Matley, and Y. T. Wong, Czech. J. Phys. 46, 85 (1996)].


[57] See the references cited in Refs. [59,61].


[68] See Chap. 8 and Appendix (Tables) of Ref. [32].


We can keep the mean temperature $T_m$ inside the convection cell constant by decreasing the top-plate (or water bath) temperature $T_t$ while increasing the bottom-plate temperature $T_b$. However, the variation of the bath temperature changes the strain on the cell holder surrounded by the bath water, leading to a slight shift of the shadowgraph image and to considerable difficulties in image processing. Furthermore, keeping $T_m$ constant does not prevent the variation of $X_m$ since the mean temperature outside the cell would be affected by the bath temperature.


96. The Nusselt number given by Ref. [38] was evaluated at the top and bottom plates. The Galerkin model for rigid boundaries gives a laterally averaged heat flux that varies slightly as a function of the vertical coordinate [95]. Thus the heat currents at the two plates are larger than the vertical mean value. A better value for comparison with the exact $\Psi = 0$ result of Schlüter et al. [94] would be a vertically and laterally averaged heat current from the eight-mode model. Then one gets $S_1 = 1.477$ for $\Psi = 0$ [St. Hollinger and M. Lücke (private communication)], closer to the value 1.422 of Schlüter et al. However, a computation of this average is somewhat involved and requires the vertical eigenfunctions of the model. Thus, for $\Psi > 0$ we used a more empirical procedure to force $S_1$ of the eight-mode model to agree with the exact result in the $\Psi = 0$ limit. It simply consisted of multiplying $S_1$ by a $\Psi$-independent factor equal to 1.422/1.718.

97. For example, C. W. Meyer, G. Ahlers, and D. S. Cannell [Phys. Rev. A 44, 2514 (1991)] found $1/g_3 = S_1 = 1.20$ [see below Eq. (2.8) of their paper] in a sample with $\sigma = 6.0$ and $\Gamma = 10$. This can be compared with the average value of 1.14 for our pure gases. We would not expect the two experimental values to agree precisely because of the different $\sigma$ and $\Gamma$.


