Demixing Due to Frictional Forces in an Electric Arc

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A description of demixing that is mathematically simple and physically transparent is introduced. The dominant demixing process at high temperatures in an atmospheric-pressure nitrogen–argon arc is predicted to be that associated with frictional forces. Spectroscopic measurements of the mass fraction distribution, which provide experimental confirmation of this demixing effect, are presented. It is shown that demixing can act to either increase or decrease the mass fraction of nitrogen as temperature increases, depending on the gas composition.

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Demixing is a diffusion-driven process that can result in spatial variations in the mass fraction of the component gases in mixtures of partially ionized or partially dissociated gases. It occurs in the presence of temperature or pressure gradients, or certain external forces such as electric fields. A temperature gradient, for example, can give rise to mole fraction gradients of the individual species present, which in turn drive diffusion of these species until the sum of all forces (such as the forces due to mole fraction gradients, frictional forces, thermal diffusion forces, and external forces) is zero.

Interest in demixing, which was extensively studied in the past [1–3], has been revived recently [4] because of the widespread application of gas mixtures in electric arcs, plasma jets, and processing plasmas.

Frie and Maecker [1,2] have classified demixing processes into a number of categories, the most important being demixing due to mole fraction (or partial pressure) gradients, frictional forces, thermal diffusion, and external forces. Consider a mixture of two gases A and B, a gas being defined as consisting of all species derived from a molecule of the gas, such as atoms, ions, and electrons derived from the ionization. Demixing due to mole fraction gradients occurs to minimize the gradients $\nabla\overline{x_A}$ and $\nabla\overline{x_B} = -\nabla\overline{x_A}$ of the mole fractions of the gases, where $\overline{x_A}$ is defined as the sum of mole fractions of all species in gas A. The bar notation indicates that a symbol refers to a gas rather than a species. In the case that the collision cross sections for interactions between all pairs of species are equal, demixing due to mole fraction gradients occurs until $\nabla\overline{x_A} = 0$. If, however, the collision cross sections are not all equal, deviations from $\nabla\overline{x_A} = 0$ will occur due to the unbalanced collisional or frictional forces acting on the different species; this effect is described as demixing due to frictional forces. Finally, further deviations from $\nabla\overline{x_A} = 0$ occur due to the effects on the different species of thermal diffusion forces and external forces.

In most cases, demixing due to mole fraction gradients is an important process. For example, at temperatures at which gas A is partially ionized but gas B is not ionized, the increase in the mole fraction of gas A with temperature as each atom is replaced by an ion and an electron leads to a flow of the gas to lower temperatures in order to minimize $\nabla\overline{x_A}$. However, in mixtures of gases with similar ionization potentials, e.g., isotopic mixtures, mole fraction gradients of the gases are negligible. Some attempts to investigate such mixtures, in which demixing due to frictional forces usually dominates, have been made; for example, Frie [1] predicted the direction of demixing in a mixture of ionizing hydrogen and deuterium. However, the complexity of the existing descriptions of demixing and the difficulty of distinguishing isotopes spectroscopically have limited the extent of such studies, and the reported experimental evidence of demixing due to frictional forces has been limited to mixtures of partially dissociated gases [5].

Here I introduce an algebraically simple and physically transparent mathematical description of demixing, based on the recently introduced combined diffusion coefficient formulation [6,7], that describes demixing in terms of gases rather than of species as in previous treatments. The equations then mirror the qualitative description given above, allowing the demixing caused by each of the processes listed to be easily distinguished. The method is applied to a mixture of nitrogen and argon, in which, as for an isotopic mixture, mole fraction gradients of the gases are negligible. It is shown that frictional forces dominate the demixing processes. Moreover, it is predicted that the direction of demixing depends on the relative mass fractions of the two gases; this is the first report of such a dependence. The predictions of the calculations are confirmed experimentally by applying a newly developed spectroscopic technique to a free-burning electric arc in a mixture of nitrogen and argon.

The number flux of the species i relative to the mass-average velocity in a gas mixture containing q species in the presence of a temperature gradient, but neglecting external forces, is given by [8,9]

$$\mathbf{g}_i \equiv n_i \mathbf{v}_i = \frac{n^2}{\rho} \sum_{j=1}^{q} m_j D_{ij} \nabla x_j - \frac{D_i^T}{m_i} \nabla \ln T, \qquad (1)$$

where $\mathbf{v}_i$ is the diffusion flux of species i relative to the mass-average velocity, D_{ij} and D_i^T are respectively the ordinary and thermal diffusion coefficients, T is the temperature, n and ρ are respectively the number density and mass density, and x_j, n_j, and m_j are respectively the mole fraction, number density, and mass of the jth species. In an ionized gas, D_{ij} and D_i^T are calculated so as to include ambipolar diffusion effects [6,9].

Murphy [6] has shown that the $\frac{1}{2}q(q-1)$ linearly independent ordinary diffusion coefficients and the $q-1$ linearly independent thermal diffusion coefficients may be replaced by a total of three combined diffusion coefficients, which describe the diffusion of two gases relative to one another. The conditions under which this can be done are that the two gases are homonuclear and do not react, and that the concentrations of the individual species depend only on the temperature and the mass fractions of the two gases. This second condition holds since the equilibration times for dissociation, ionization, and recombination reactions are typically around 2 orders of magnitude shorter than diffusion times; a chemical equilibrium description is thus valid.

The combined diffusion coefficients are defined by an expression for the number flux of gas A, of equivalent form to that of Eq. (1) for a two-species gas:

$$\overline{\mathbf{g}_A} = \frac{n^2}{\rho}\overline{m_B}\,\overline{D_{AB}^x}\nabla\overline{x_B} - \frac{(\overline{D_{AB}^{T1}} + \overline{D_A^T})}{\overline{m_A}}\nabla \ln T, \tag{2}$$

where $\overline{m_B}$ is the average mass of the heavy species of gas B. Murphy [6] has derived the following expressions for the combined diffusion coefficients:

$$\overline{D_{AB}^x} = \frac{1}{\overline{m_B}}\sum_{i=2}^{p} s_i \sum_{j=1}^{q} m_j D_{ij}\frac{\partial x_i}{\partial \overline{x_B}}, \tag{3}$$

$$\overline{D_{AB}^{T1}} = -\frac{n^2\overline{m_A}}{\rho}\sum_{i=2}^{p} s_i \sum_{j=1}^{q} m_j D_{ij} T\frac{\partial x_j}{\partial T}, \tag{4}$$

and

$$\overline{D_A^T} = \overline{m_A}\sum_{i=2}^{p}\frac{s_i D_i^T}{m_i}, \tag{5}$$

where the s_i are stoichiometric coefficients and where species 1 is the electron, species 2 to p belong to gas A, and species $p+1$ to q belong to gas B.

The equilibrium mole fraction gradients of the two gases are calculated by setting $\overline{\mathbf{g}_A} = 0$ in Eq. (2), giving

$$\nabla\overline{x_B} = -\nabla\overline{x_A} = \frac{\rho}{n^2}\frac{(\overline{D_{AB}^{T1}} + \overline{D_A^T})\nabla \ln T}{\overline{m_A}\,\overline{m_B}\,\overline{D_{AB}^x}}. \tag{6}$$

Setting $\overline{D_{AB}^{T1}} = \overline{D_A^T} = 0$ gives $\nabla\overline{x_B} = \nabla\overline{x_A} = 0$, which is simply the condition that mole fraction gradients have vanished; hence demixing due to mole fraction gradients is described by the remaining nonzero diffusion coefficient $\overline{D_{AB}^x}$, which shall be termed the combined mole fraction diffusion coefficient. Also, Eq. (5) shows that the term in the combined thermal diffusion coefficient $\overline{D_A^T}$ describes demixing due to thermal diffusion. The remaining diffusion coefficient, $\overline{D_{AB}^{T1}}$, which shall be termed the temperature diffusion coefficient, describes demixing due to the remaining phenomena treated in the equations, that is, due to frictional forces. Hence, each of the diffusion coefficients in Eqs. (2) and (6), corresponds to a distinct demixing process.

I now apply this treatment of demixing to a mixture of argon and nitrogen. The diffusion coefficients are calculated as a function of temperature and the relative mass fractions of the two gases as in Ref. [6]. Figure 1 shows the equilibrium mole fractions of the main species in a mixture of nitrogen and argon in the absence of temperature gradients. It can be seen that the mole fraction of each gas is essentially independent of temperature for $T > 8000$ K, since at any given temperature, both argon and nitrogen are ionized to the same degree. Demixing due to mole fraction gradients will thus be a relatively minor effect for $T > 8000$ K.

Figure 2 shows the temperature dependence of the three combined diffusion coefficients for different mixtures of argon and nitrogen. $\overline{D_{\mathrm{Ar,N}}^x}$ is only weakly dependent on gas composition, and is always positive. In contrast, $\overline{D_{\mathrm{Ar,N}}^{T1}}$ and $\overline{D_{\mathrm{Ar}}^T}$ are strongly dependent on gas composition. At temperatures between about 10 000 and 20 000 K, $\overline{D_{\mathrm{Ar,N}}^{T1}}$ is negative for small argon mass fractions, positive for large argon mass fractions, and small for intermediate mass fractions. $\overline{D_{\mathrm{Ar}}^T}$ is always small. Note that a discrepancy exists between the data shown in Fig. 2(b)

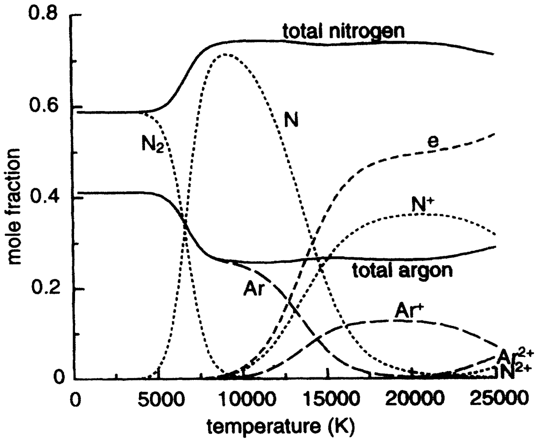

FIG. 1. Equilibrium mole fractions in a mixture of 50% argon and 50% nitrogen by weight at a pressure of 101.3 kPa, neglecting demixing effects. Species with mole fractions less than 0.01 over the full temperature range are not shown. The total mole fractions of argon and nitrogen include electrons derived from the ionization of the respective gases.

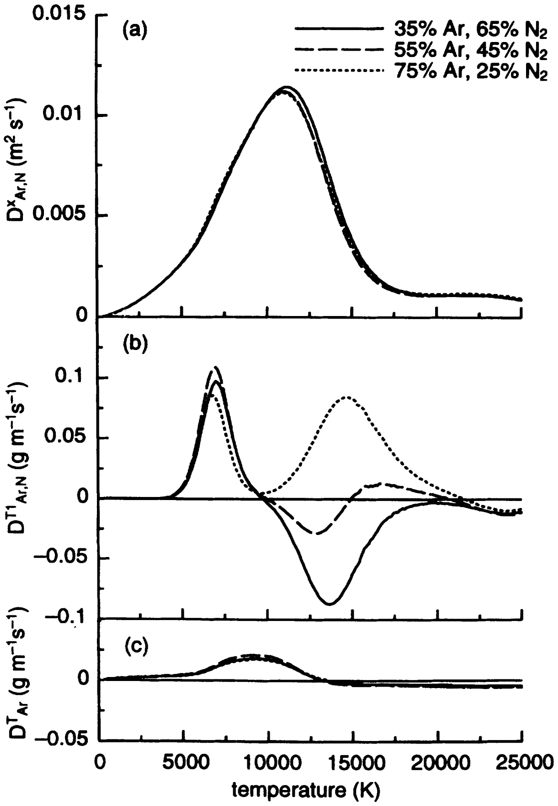

FIG. 2. Combined diffusion coefficients for different mixtures of argon and nitrogen by weight. (a) Mole fraction diffusion coefficient; (b) temperature diffusion coefficient; (c) thermal diffusion coefficient.

and those given in Fig. 6. of Ref. [6] for $T < 10\,000$ K; this is due to an error in the latter figure.

Reference to Eq. (6) in the light of the foregoing discussion shows that the sign of the mass fraction gradient in a mixture of partially ionized argon and nitrogen in equilibrium will depend on the mass fractions of the two gases. Hence, the mass fraction of argon is predicted to increase with temperature when the mass fraction of argon is much less than that of nitrogen, and to decrease with temperature in the opposite case.

To test this prediction, and to investigate demixing due to frictional forces generally, measurements of the composition and temperature of a free-burning arc in different mixtures of argon and nitrogen were performed. The arc geometry is typical of that used in gas–tungsten arc welding: the arc was struck at atmospheric pressure between a conical thoriated-tungsten cathode (60° included angle) and a flat water-cooled anode consisting of a 12.7 mm diam, 5 mm thick tungsten disk brazed into a copper plate of equal thickness. The tungsten disk was eroded by the arc sufficiently slowly that the arc properties were not altered during the measurements [10]. The cathode tip was 5 mm above the anode, and the arc current was 200 A. The argon and nitrogen were fully mixed before being directed through a nozzle concentrically surrounding the top of the cathode. The measurements were performed using a spectroscopic technique based on the Fowler–Milne method, which is widely used for temperature measurements of arcs burning in pure gases [11]. The arc was scanned horizontally across the axis of the optical system; at each position, the intensity of emission of a spectral line, integrated along a chord through the arc, was measured. A similar scan of the continuum intensity was made and this value subtracted from the line intensity. The data were then converted to a radial distribution by Abel inversion.

The spectroscopic technique required measurement of the emission coefficient of both an argon line (the 727.3 nm Ar I line) and a nitrogen line (the 746.8 nm N I line); these spectral lines were selected because they show weak self-absorption, and are well separated from other lines. The measured argon and nitrogen emission coefficients in the argon–nitrogen arc were respectively normalized to the maximum emission coefficients measured in arcs burning in pure argon and pure nitrogen. A given pair of measured emission coefficients corresponds to two possible mass-fraction and temperature combinations. This ambiguity is resolved by requiring that temperature increases towards the center of the arc. A full description of the measurement technique will be given in a later publication.

Figure 3 shows the measured radial dependence of the mass fraction of argon 2 mm axially below the cathode for three different input flows of argon and nitrogen. This axial position is sufficiently far from the cathode for radial

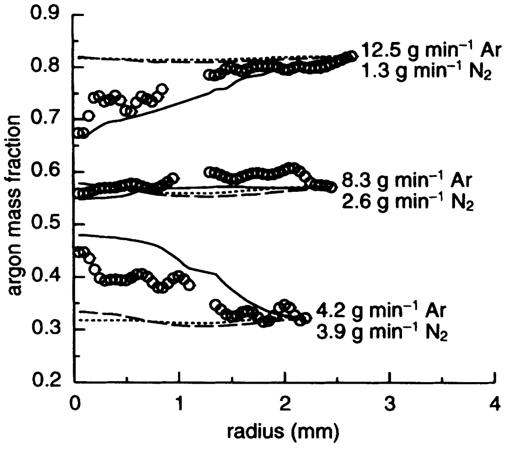

FIG. 3. Radial dependence of the mass fraction of argon in a free-burning arc 2 mm below the cathode, in three different mixtures of argon and nitrogen. The input mass flow rates of nitrogen and argon are given. ○: experiment; solid line: calculated using Eq. (6); broken line: calculated using Eq. (6) with $\overline{D_{AB}^{T1}} = 0$; dotted line: calculated using Eq. (6) with $\overline{D_{AB}^{T1}} = \overline{D_A^T} = 0$.

electric fields and radial convective flows to be negligible [12], and for sufficient diffusion to have taken place for demixing to be apparent despite the large convective flows axially downward from the cathode. Thus, the equilibrium description of demixing in Eq. (6) should be a reasonably accurate representation of the radial mole fraction profiles, particularly at larger radii where the flow velocities are smaller.

The changes in mass fraction with radius shown in Fig. 3 demonstrate a substantial degree of demixing. These results are compared with three sets of calculated curves. The first is calculated using Eq. (6), and thus takes into account demixing due to mole fraction gradients, thermal diffusion, and frictional forces. The second set is obtained by setting $\overline{D_{AB}^{T1}} = 0$ in Eq. (6), thereby neglecting diffusion due to frictional forces. The third set is obtained by setting $\overline{D_{AB}^{T1}} = \overline{D_A^T} = 0$ in Eq. (6), and thus corresponds to demixing due to mole fraction gradients only. The calculated curves are derived by numerical integration in one dimension, using the measured temperature profiles. The integration is started using the measured mass fraction of argon corresponding to $T = 10\,500$ K, since the measurements are not possible below this temperature, owing to the low level of emitted radiation and deviations from local thermodynamic equilibrium that render the Fowler–Milne technique invalid [13]. Note that the measured mass fraction of argon at $T = 10\,500$ K differs significantly from the mass fraction in the input gas mixture; this is a consequence of demixing associated with the dissociation of nitrogen, which occurs at temperatures around 7000 K. The integration continues radially inwards to the arc axis, where the temperature is measured to be 20 100, 18 800, and 18 400 K for the three cases shown in Fig. 3, the temperature being larger for higher nitrogen concentrations.

Figure 3 confirms that demixing due to mole fraction gradients and due to thermal diffusion is small. When, however, frictional force effects are included in the calculations, demixing of a similar magnitude to that measured in the experiment is exhibited. This is strong evidence that demixing due to frictional forces is the dominant demixing effect in this case. Moreover, the experimental results confirm the predicted dependence of the direction of demixing on the relative concentration of argon and nitrogen.

In summary, I have introduced a new, mathematically simple and physically transparent description of demixing based on the combined diffusion coefficient formulation. This description has been applied to a mixture of nitrogen and argon. To test the predictions of the calculations, a spectroscopic technique that allows measurement of mass fraction and temperature distributions in gas mixtures has been developed and applied to a free-burning arc. The substantial demixing that was measured has been shown, by comparison with the calculations, to be almost wholly due to frictional forces. Moreover, the measurements confirm that demixing can act to increase or to decrease the mass fraction of nitrogen as temperature increases, depending on the initial mass fraction of nitrogen.

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