Modelling and diagnostics of plasma chemical processes in mixed-gas arcs

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Abstract: The characterisation of thermal plasmas derived from gas mixtures is considered. The assumption of local chemical equilibrium is used to derive the combined diffusion coefficient formulation, which greatly simplifies the treatment of diffusion in mixtures of non-reacting homonuclear gases. The formulation is applied to the modelling of demixing in free-burning arcs. A two-dimensional numerical model is used to assess the relative importance of different demixing processes in argon–helium and argon–nitrogen arcs. Demixing is found to strongly alter the composition of these arcs. The predicted arc compositions are shown to agree well with measurements performed by spectroscopic techniques. A comparison of laser-induced fluorescence measurements of atomic hydrogen density in an argon–hydrogen arc with calculations shows that the assumption of local chemical equilibrium is not valid in the fringes of such an arc.

Introduction

Most investigations in the thermal plasma field have focussed on the relatively simple case of plasmas derived from a single gas. If, as is usual, it is assumed that the plasma is in local thermodynamic equilibrium, it is possible to characterise the temperature and composition of such plasmas by measuring the emission from one spectral line. Under the same assumption, the plasma can be numerically modelled without considering diffusion or chemical reactions.

Most industrial plasmas, however, are derived from mixtures of gases. Mixtures of argon and gases such as helium, hydrogen, oxygen, carbon dioxide and nitrogen are used in welding and plasma spraying, for example. Impurities derived from vaporisation of the workpiece, droplets or spray particles may also be present. In processes such as plasma waste destruction, very complex gas mixtures occur.

Plasmas in gas mixtures are considerably more difficult to characterise than single-gas plasmas, since the occurrence of demixing, the diffusive separation of the component gases, means that the gases cannot be assumed to be uniformly distributed. While it is often reasonable in modelling of mixed-gas plasmas to assume local chemical equilibrium (LCE), thereby defining the composition of the plasma given the local chemical element concentrations and temperature, it is still necessary to consider diffusion, since it is diffusion that determines the local chemical element concentrations.

Diffusion is the most difficult transport process to treat. In contrast to viscosity, thermal conductivity and electrical conductivity, each of which is respectively described by a single coefficient, a total of $(q^2 - q)/2$ ordinary diffusion coefficients and $q - 1$ thermal diffusion coefficients have to be calculated for each temperature and composition in a gas mixture containing q species. The recently introduced combined diffusion coefficient formulation (1) allows these $(q^2 + q - 2)/2$ diffusion coefficients to be replaced by just three in many binary gas mixtures without loss of accuracy. This greatly simplifies the treatment of a wide range of important phenomena, such as vaporisation of metal electrodes and droplets in arcs, and demixing in many mixed-gas arcs.

In this paper, I briefly summarise the combined diffusion coefficient formulation, and outline its application to demixing. A two-dimensional model of a free-burning arc that incorporates the combined diffusion coefficient formulation is used to calculate the influence of demixing on arcs in mixtures of argon and nitrogen, and argon and helium. The predicted compositions and temperatures are compared with experimental results. Finally, the limitations of the assumption of LCE are investigated by comparing laser-induced fluorescence measurements of atomic hydrogen densities in an argon–hydrogen arc with calculated densities.

Combined diffusion coefficients

The combined diffusion coefficient formulation can be applied to a mixture of homonuclear non-reacting gases in LCE. The formulation's essential feature is that diffusion of gases, rather than of species, is treated. Here a gas is defined to consist of all species derived from that gas; hence nitrogen gas includes nitrogen molecules, atoms, ions and electrons derived from ionisation of these species.

In a gas mixture containing q species, the equation describing the number flux of species i relative to the mass-average velocity in the presence of a temperature gradient, but neglecting external forces and gradients in the total pressure, is given by (2, 3)

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

where $\mathbf{v}_i$ is the diffusion velocity of species i relative to the mass-average velocity, 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 ionised gas, the ordinary and thermal diffusion coefficients, D_{ij} and D_i^T respectively, are calculated so as to include ambipolar diffusion.

If we consider a mixture of two gases, with species 1 being the electron, species 2 to p belonging to gas A, and species $p + 1$ to q belonging to gas B, we can define the number flux of gas A as $\overline{\mathbf{g}_A} = \sum_{i=2}^{p} s_i \mathbf{g}_i$, where the s_i are stoichiometric coefficients, defined in Ref. (1). Then by writing an expression for $\overline{\mathbf{g}_A}$ in a form analogous to Eq. 1:

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

where $\overline{m_B}$ is the average mass of the heavy species of gas B and $\overline{x_B}$ is the sum of mole fractions of all species of gas B, it is possible (1) to derive expressions for the combined diffusion coefficients $\overline{D_{AB}^x}$, $\overline{D_{AB}^{T1}}$ and $\overline{D_A^T}$. $\overline{D_{AB}^x}$ and $\overline{D_{AB}^{T1}}$ are weighted averages of the ordinary diffusion coefficients D_{ij}, and $\overline{D_A^T}$ is a weighted average of the thermal diffusion coefficients D_i^T.

Demixing

Frie and Maecker (4, 5) classified demixing processes into a number of categories, the most important being demixing due to mole fraction (or partial pressure) gradients, frictional forces and thermal diffusion. In a mixture of two gases A and B, demixing due to mole fraction gradients occurs to minimise $\nabla \overline{x_A}$ and $\nabla \overline{x_B} = -\nabla \overline{x_A}$. Deviations from $\nabla \overline{x_A} = 0$ occur because the collision cross sections for interactions between the different pairs of species are not equal, thus leading to unbalanced collisional or frictional forces acting on the different species; this is referred to as demixing due to frictional forces. Further deviations from $\nabla \overline{x_A} = 0$ occur due to thermal diffusion forces.

Each of the combined diffusion coefficients in Eq. 2 corresponds to one of these demixing processes (6). The term in the coefficient $\overline{D_{AB}^x}$ describes demixing due to mole fraction gradients. This can be seen by setting $\overline{D_{AB}^{T1}} = \overline{D_A^T} = 0$ and $\overline{\mathbf{g}_A} = 0$ in Eq. 2; the latter condition implies that diffusive processes have reached equilibrium. Equation 2 then becomes $\nabla \overline{x_B} = 0$, which is simply the condition that mole fraction gradients have vanished. Further, the term in $\overline{D_A^T}$ describes demixing due to thermal diffusion, since $\overline{D_A^T}$ is a weighted average of the thermal diffusion coefficients. The term in the remaining diffusion coefficient, $\overline{D_{AB}^{T1}}$ describes demixing due to the remaining process treated in the equations, that is, due to frictional forces.

A two-dimensional model of demixing in a free-burning arc

The treatment of demixing described in the previous section has been incorporated in the two-dimensional axisymmetric free-burning arc model of Lowke et al. (7). Two changes were required to make the model applicable to a mixture of two gases: an equation for the conservation of mass of one of the gases had to be included, and the conservation of energy equation had to be modified to account for the change in enthalpy when the mass fractions of the gases were altered. The mass conservation equation for gas A is

$$\nabla \cdot (\overline{\rho_A} \mathbf{v}) + \nabla \cdot (\overline{m_A} \overline{\mathbf{g}_A}) = 0, \tag{3}$$

where $\overline{\rho_A}$ is the mass density of gas A. This was written in terms of the mass fraction of gas A by using Eq. 2 and noting that $\overline{\rho_A} = \rho \overline{Y_A}$ and $\overline{x_A} = \overline{M} \overline{Y_A} / \overline{M_A}$, where $\overline{M}$ and $\overline{M_A}$ are the average mass of all
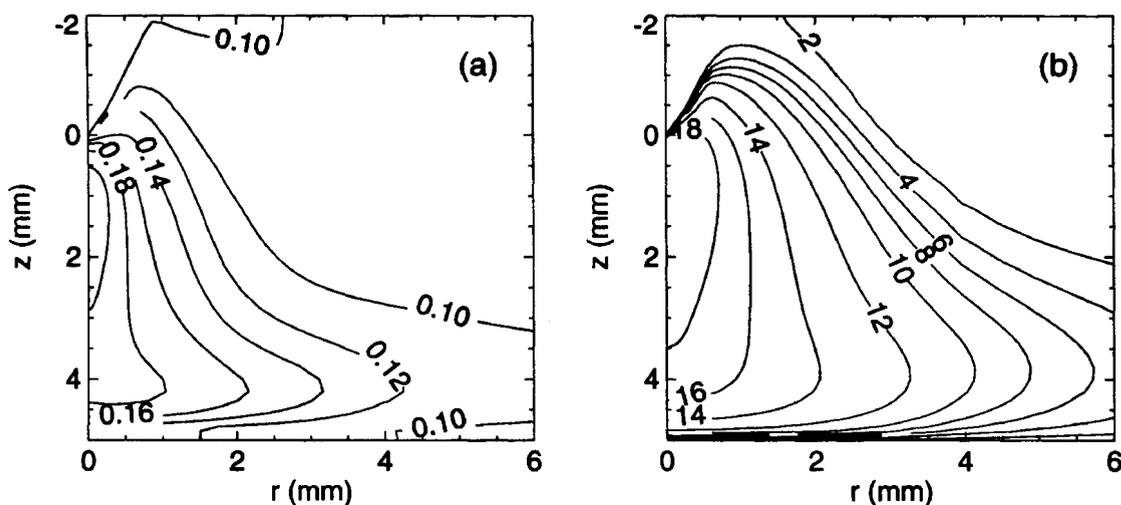
Figure 1: (a) Isopleths of helium mass fraction and (b) isotherms, labelled in units of 1000 K; calculated for a 200 A arc in a mixture of 90% argon and 10% helium by mass.

particles (including electrons) in the gas mixture and in gas A respectively. The energy conservation equation given by Lowke *et al.* (7) was modified by including the terms on the left-hand side of Eq. 3 multiplied by Δh, where Δh is the difference between the enthalpy of gas A and the enthalpy of gas B. In addition, a term $(5k_B/2ec_p)j\nabla h$, where k_B is Boltzmann's constant, e is the electronic charge, c_p is the specific heat, j is the current density and h is the enthalpy, was included. This term describes energy transfer due to electron flow and is generally included in arc models.

An arc typical of those used in gas–tungsten arc welding, with a conical cathode of 60° included angle situated 5 mm above a flat anode, was modelled. The arc current was 200 A, and the total gas flow was 10 L min^{-1} unless otherwise noted. The gas mixture was input through a nozzle concentrically around and with radius 2.35 mm greater than the cathode. The gas composition at the top boundary, at the cathode and at the radial edge boundary was set equal to the input composition. A gradient boundary condition was used at the anode.

Calculations were performed for arcs in mixtures of argon and helium and of argon and nitrogen. The transport coefficients, including combined diffusion coefficients, used for argon–nitrogen mixtures were those given by Murphy and Arundell (8). Transport coefficients for argon–helium mixtures were calculated in the same manner, using collision integrals similar to those given by Pateyron *et al.* (9). Net radiation emission coefficients for argon and helium were calculated by the method of Cram (10); those for nitrogen were taken from Ernst *et al.* (11) for a radius of 1.5 mm. These latter data were multiplied by a factor of 1.5 because the radius of the radiating central region of the arc is less than 1.5 mm (12).

Figure 1 shows the calculated temperature and mass fraction contours for an arc in a mixture of 90% argon and 10% helium by mass. It is clear that demixing acts to strongly concentrate helium in the arc centre. Figure 2(a) shows the contributions of the different demixing processes at a position 2 mm below the cathode. Demixing due to mole fraction gradients, calculated by setting $\overline{D_{AB}^{T1}} = \overline{D_A^T} = 0$ in Eq. 2, is found to increase the helium mass fraction as the radius decreases, with a small decrease in the central 1 mm. This occurs because argon ionises at a lower temperature than helium: in the absence of demixing, $\overline{x_{Ar}}$ increases with temperature from 7000 to 17 000 K as each argon atom is replaced by an argon ion and an electron, and then decreases when temperature is increased further as the helium atoms ionise. Demixing due to mole fraction gradients acts to counter these changes in $\overline{x_{Ar}}$. Demixing due to frictional forces, whose effect in addition to that of mole fraction gradients is calculated by setting $\overline{D_A^T} = 0$ in Eq. 2, acts to further concentrate helium in the arc centre. The relatively small effect of demixing due to thermal diffusion, which corresponds to the difference between the solid and dashed curves in Fig. 2(a), is in the same direction as demixing due to frictional forces.
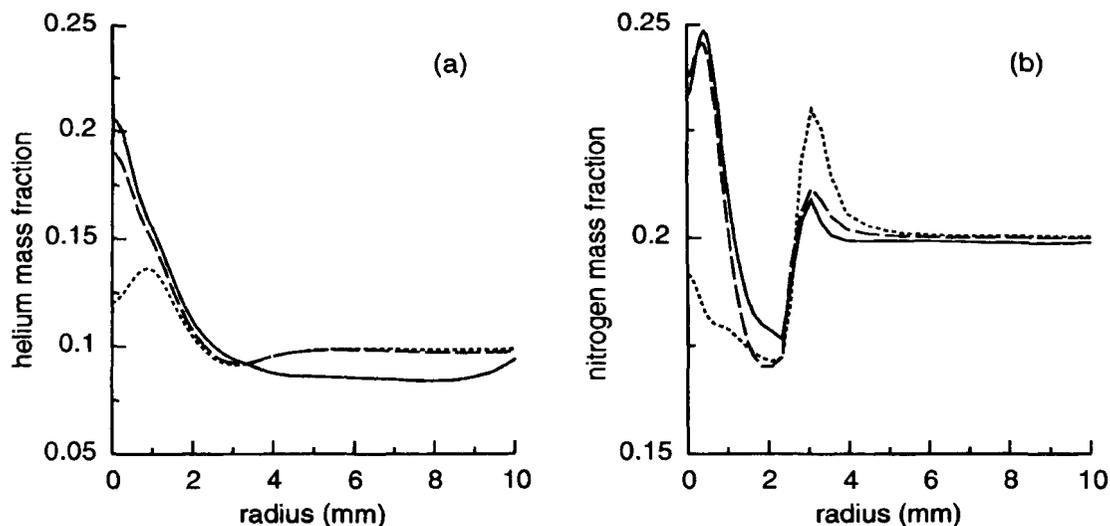
Figure 2: Calculated radial dependence of the mass fraction of the minority gas 2 mm below the cathode in a free-burning arc in a mixture of (a) 90% argon and 10% helium by mass, (b) 80% argon and 20% nitrogen by mass. ——: all demixing effects considered; · · ·: demixing due to mole fraction gradients only; — — —: demixing due to mole fraction gradients and frictional forces only.

The contributions to demixing in an arc in a mixture of 80% argon and 20% nitrogen are shown in Fig. 2(b). In this case, demixing due to mole fraction gradients leads to a decrease in the nitrogen mass fraction at radii less than that of the dissociation temperature of molecular nitrogen (about 6400 K, corresponding to a radius of 2.7 mm), since demixing acts to counter the increase in $\overline{x_N}$ due to dissociation. It has little further effect in the central region of the arc, since argon and nitrogen atoms ionise at similar temperatures. The dominant demixing process in the central region is that due to frictional forces, which acts to concentrate nitrogen in the arc centre in this case. In the central 0.5 mm, the nitrogen mass fraction decreases towards its input value because the axial convective velocity of the gas mixture is so large on axis that diffusion is not sufficiently rapid to cause complete demixing. This effect is not seen in the argon–helium arc since diffusion is much more rapid and the convective velocity is lower in this case.

Comparison with measurements

Spectroscopic determination of temperature and composition of mixed-gas arcs requires the measurement of the emission of spectral lines associated with at least two different species. Murphy (13) has developed a technique based on the Fowler–Milne method, which has been widely used to measure temperature in single-gas arcs, and has applied it to arcs in argon–nitrogen mixtures. It was observed that demixing could cause either an increase or decrease in the nitrogen mass fraction in the central region of the arc depending on the composition of the input gas mixture. This effect was explained (6) using a one-dimensional model of demixing based on Eq. 2. In Fig. 3, the measurements of nitrogen mass fraction and temperature are compared with the predictions of the two-dimensional arc model. The input gas mixtures used in the model differ from the input flow rates given in Ref. (6), since it has been found that the nitrogen flow rates were underestimated by a factor of approximately two.

The agreement between the calculations and the measurements is generally good. In particular, the calculations indicate, in agreement with the measurements, that demixing increases the mass fraction of nitrogen in the central region of the arc when more argon than nitrogen is present, and decreases the mass fraction of nitrogen when more nitrogen than argon is present. The calculated temperatures decrease more rapidly towards the edge of the arc than the measured profiles. The calculated mass fraction profiles are correspondingly radially compressed with respect to the measured profiles. It was not possible to experimentally confirm the effects of convection in the central 0.5 mm of the arc that were discussed in the previous section because of the large uncertainties in the results in this region; these uncertainties arose because the errors associated with Abel transforms, which were required to analyse the spectroscopic data, accumulate near the arc axis.
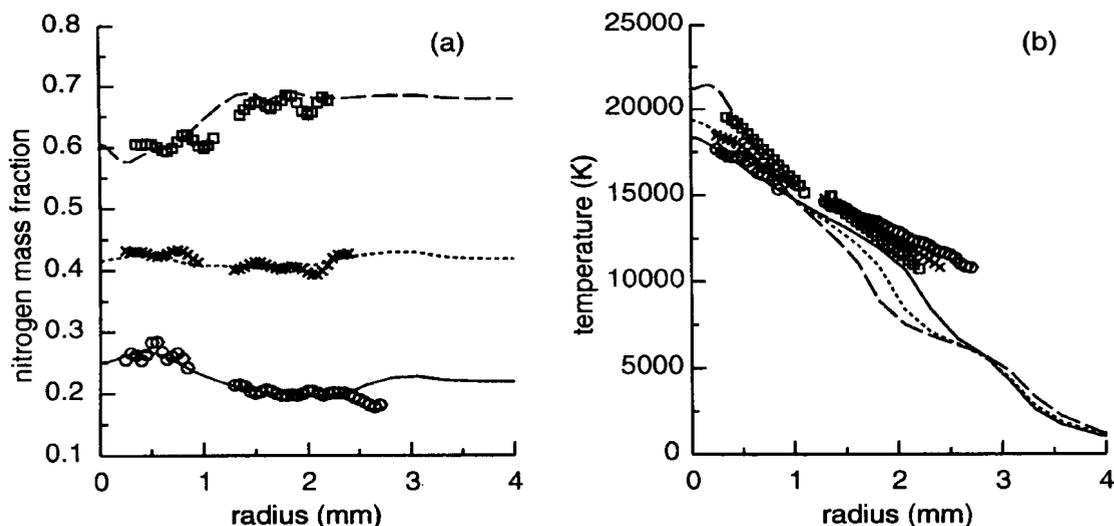
Figure 3: Radial dependence of (a) mass fraction of nitrogen and (b) temperature, at a position 2 mm below the cathode in 200 A free-burning arcs in mixtures of argon and nitrogen. Measurements are shown by symbols and two-dimensional model calculations by curves. o, —: 78% argon, 22% nitrogen, 11.0 Lmin^{-1} total flow; ×, · · ·: 59% argon, 41% nitrogen, 10.5 Lmin^{-1} total flow; □, — — —: 32% argon, 68% nitrogen, 10.1 Lmin^{-1} total flow; all proportions are by mass.

Hiraoka (14) has performed measurements of demixing in argon–helium arcs; his values of arc composition on axis are in good agreement with the predictions of the model.

Deviations from LCE in an argon–hydrogen arc

Snyder *et al.* (15) have recently performed laser-induced fluorescence measurements of atomic hydrogen density in a free-burning argon–hydrogen arc. Figure 4 shows a comparison of the measured density, assumed to be proportional to the fluorescence signal, with the density calculated using the one-dimensional LCE model of demixing introduced in Ref. (6). The atomic hydrogen density peaks

at a radius corresponding to a temperature of about 4000 K, just above the dissociation temperature of hydrogen. The measured density decreases more rapidly than the calculated density towards the arc centre, and less rapidly towards the arc edge. The first discrepancy is due to Stark broadening of the detected H$_\alpha$ emission, which leads to the emission being much broader than the detector bandwidth in the central region, so only a fraction of the total fluorescence signal is detected. The second discrepancy can be attributed to the rapid radial diffusion of atomic hydrogen. Calculations (15) based on Eq. 1 indicate that at radii greater than that of the density peak, the diffusion rate of atomic hydrogen is much greater than its rate of recombination to form molecular hydrogen. This leads to an increase in the atomic hydrogen density in the edge region relative to that predicted assuming LCE.

To model the region at the edge of the argon–hydrogen arc accurately would require the consideration of deviations from LCE: the diffusion
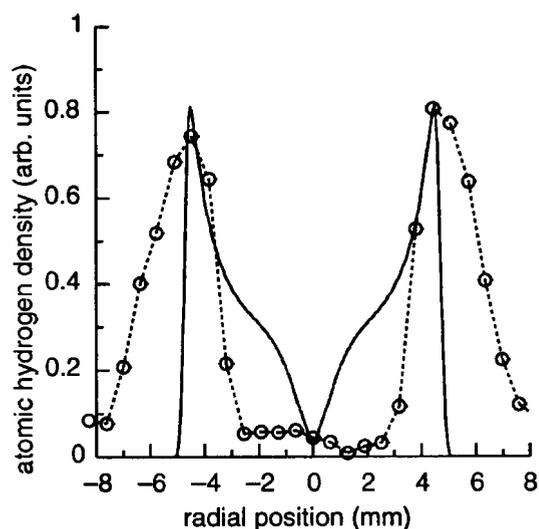

Figure 4: Radial dependence of the atomic hydrogen density 1 mm below the cathode in a 200 A free-burning arc, in a mixture of 0.26% hydrogen and 99.74% argon by mass with 8 Lmin^{-1} total flow. o, · · ·: LIF measurements; —: calculation assuming LCE.

of atomic hydrogen and molecular hydrogen would have to be calculated separately, and the recombination and dissociation reactions would have to be explicitly included. The approach used above in modelling argon–helium and argon–nitrogen arcs would thus not be valid, although a model based on the LCE assumption may still be accurate in the hotter regions of the arc, where reactions proceed more rapidly. Note that deviations from LCE in argon–nitrogen arcs are expected to much smaller that in argon–hydrogen arcs, since the diffusion rate of nitrogen atoms is approximately an order of magnitude smaller than that of hydrogen atoms. Dissociation and recombination reactions are of course not relevant to argon–helium arcs.

Conclusions

Plasmas in mixtures of gases are more difficult to model than single-gas plasmas because of the increased importance of chemical reactions and diffusion. By assuming local chemical equilibrium, the need to consider chemical reactions is dispensed with. Further, the treatment of diffusion can be dramatically simplified in mixtures of non-reacting homonuclear gases in LCE using the combined diffusion coefficient formulation, making possible accurate modelling of plasmas in many gas mixtures.

The combined diffusion coefficient formulation is well suited to investigating demixing, with the different combined diffusion coefficients corresponding to distinct demixing processes. The relative importance of these processes in argon–helium and argon–nitrogen mixtures has been assessed using a two-dimensional numerical model of a free-burning arc. The calculations demonstrate that demixing has a large effect on the composition of the arcs.

The plasma compositions and the temperatures predicted by the model are in good agreement with spectroscopic measurements of argon–nitrogen arcs; in particular the prediction that the direction of demixing depends on the relative concentrations of argon and nitrogen was confirmed.

Finally, by comparing laser-induced fluorescence measurements of atomic hydrogen density in an argon–hydrogen arc with calculations, it was found that atomic hydrogen has anomalously high concentrations in the fringes of the arc. This was attributed to deviations from LCE due to diffusion of atomic hydrogen proceeding more rapidly than recombination reactions in this region. Such effects are not expected to lead to significant departures from LCE in arcs in other gas mixtures.

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