Self-Diffusion in Liquid Elements

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With increasing insight into transport and segregation in solidification and crystal growth, reliable data for diffusivities in liquid metals and semiconductors have become essential for guidance in process development. However, at this point even self-diffusion in elemental liquids is not well understood. In particular, there is little insight into the temperature dependence of diffusivities and its correlation to the temperature-dependent liquid structure of an element. Currently, the differences between several theoretical predictions are often less than those between different sets of data for the same system. Hence, for both theoretical and technological developments, there is a clear need for diffusivity measurements of improved accuracy and precision for a large variety of elements over wide temperature ranges.

Based on the methodology of Codastefano, Di Russo, and Zanza [*Rev. Sci. Instrum.*, vol. 48, p 1650 (1977)], we have developed a technique for the *in situ* measurement of diffusivities in liquids at several temperatures with one sample. In this approach, which circumvents solidification of the diffusion sample prior to concentration profiling, the evolution of the concentration distribution of a radiotracer is followed in real time using two pairs of radiation detectors.

In experiments with ^{114m}In/In and ^{125}Te/Te, apparent self-diffusivities were obtained, on the ground, between 200 °C and 900 °C (540 °C and 740 °C for Te) with an uncertainty of ± 5%. By utilizing the different self-absorption characteristics of the 24- and 190-keV photons of ^{114m}In and ^{125}Te, transport in the bulk of the sample and near the container wall was investigated independently. No difference was found.

The self-diffusivity of ^{114m}In/In was determined at 185 °C in low-gravity as a risk mitigation experiment (NASA-*Mir* Increment 4). While the diffusivities obtained at low-gravity were within the uncertainty range of our ground results, the results for the three runs are within 0.5 % of each other. This narrowing of the data range is consistent with other investigators results. Again, no difference was found for “surface” or “bulk” diffusivity results.

Two-dimensional numerical simulations of the effect of blockages and/or bubbles on diffusion profiles of long capillaries were performed. In addition, the effect of a nonuniform radial diffusivity on the concentration profile was calculated. This was done for both the long capillary technique and the real-time methodology of Codastefano *et al.* These methods are believed to require a 1-D diffusion profile being maintained throughout the experiment. For both methods we modeled blockages of up to 75% of a 3 mm high 1 mm long source in a 30 mm long cell and 1 mm bubbles/voids placed at various locations along the samples outer surface. “Radial” nonuniformities of up to 10 times the input diffusivity over 300 µm (10% of the sample width)

were also modeled. These simulations showed that after a short time period the overall concentration fields are not significantly disrupted, except for an unrealistic, 75% blockage using the long capillary technique. Hence, we were able to reproduce the input diffusivity within a few percent. This implies that any measurable nonuniformity in the concentration field is not due to a disruption of the diffusion path.

We have numerically assessed the effect of buoyancy-driven convection in vertical, liquid-filled diffusion capillaries with (small) azimuthal thermal asymmetries. Calculations of the 3D-time dependent transport, based on the properties of liquid indium at 1000 K, yielded a variety of results with practical implications. We found that with horizontal temperature nonuniformities across the sample as low as 1 and 0.1 °C, respectively, convective transport in capillaries of 1 and 3 mm diameter can exceed diffusive transport. More sobering, temperature nonumiformities of a few hundredths of a degree can result in significant convective contamination. Superimposed vertically "stabilizing" temperature gradients did not sufficiently reduce these convective transport contributions. Hence, the widely used approach of keeping the top of the capillary slightly warmer than the bottom appears to be an ineffective means of "preventing convection." Most striking, we found that diffusive-convective transport can result in axial concentration profiles that are analytically indistinguishable from pure diffusion profiles. This casts considerable doubt on various graphical criteria previously used to demonstrate the absence of significant convective contamination in diffusivity data.