On diffusion in heterogeneous media

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Diffusion in heterogeneous media has been investigated for over forty years. However, the derived equations for bulk (effective) diffusivity in multi-phase systems were mostly incorrect because of the use of an inappropriate similarity between diffusion and other physical properties such as thermal conductivity. The mistake has permeated through the literature and textbooks. Specifically, the role of concentration partitioning between different phases in diffusion was not considered in such similarity relations. In this work, we present the correct method to derive such relations in heterogeneous media.

Barrer [1] used the similarity between diffusivity and thermal conductivity to derive the relation between the bulk (effective) diffusivity and the individual-phase diffusivities. The approach was followed by many others [2-4]. Unfortunately the similarity approach by Barrer [1] is incorrect because there is also dissimilarity. The key difference is that, even though heat conduction and mass diffusion are characterized by a similar flux equation ($\mathbf{J}_{heat} = -k\nabla T$ for heat conduction and $\mathbf{J}_{mass} = -D\nabla C$ for diffusion), in heat conduction, T is continuous across phase boundaries, whereas in diffusion, C is usually not continuous across phase boundaries. The concentration in each phase plays a major role in controlling the contribution by the phase to the bulk diffusive flux and hence the bulk diffusivity. For example, if the concentration of a component in a phase is very low, even if the diffusivity in the phase is high, the contribution of diffusion in that phase to the bulk diffusion flux can still be negligible. Hence, previous models for diffusivity in composite materials or multi-mineral rocks, no matter how sophisticated, are fundamentally wrong because the foundation is a mistake.

Correcting the mistake is straightforward. Write the mass flux in terms of chemical potential and mobility [5]:

$$\mathbf{J}_{mass} = -M\nabla\frac{\mu}{RT},$$

where M is mobility, μ is chemical potential, R is the universal gas constant, and T is absolute temperature. Because $\mu/(RT)$ is continuous across phase boundaries, the relation between bulk mobility and individual-phase mobilities is the same as that between bulk heat conductivity and individual-phase heat conductivities. That is, all previous relations for diffusion cannot be directly applied to diffusivities, but can be applied to mobilities. Then, from the relation between diffusivity and mobility: $D_i = M_i/C_i$ (ignoring nonideality, [5,6]), where C is concentration and subscript i indicates the phase or the bulk system, the correct relations can be obtained, which will be presented.

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Probing quartz (101) surface structure in water with X-ray scattering method

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Knowledge of the atomic level structures at the quartz water inteface will be a crutial component for understanding the behavior of such surface during the dissolution/precipitation processes. An earlier study probed the interfacial structure of quartz (101) and (100) surface in water along the surface normal direction [1]. Our prevoius work revealed the 3D interfacial structures at the single crystal quartz (101)–deionized water interface, including the relaxations of the atoms in the near surface region and the distribution of the interfacial water molecules [2]. In this study, a different interfacial structure was observed at the quartz (101)-water interface with high resolution surface X-ray scattering method (i.e., crystal truncation rod). This might indicate a different terminations of the surface when in contact with water. The detail structure information of quartz surface in water would be an important first step in revealing the reaction paths of the dissolution/precipitation processes when exposed to aqueous solutions at various conditions.

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