Variational formulation of the steady diffusion model of a reaction zone

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This paper reformulate the steady diffusion model originally formulated by Fisher (1973) and Joesten (1978), to include coupling effects among diffusive flows and to describe properly the movement of the interstitial fluid. Variational principle for the condition of minimum entropy production rate is employed to define the steady state where non-fixed thermodynamic force and its conjugate flux will disappear. The variational formulation with volume-fixed (constant porosity) reference frame shows that cross coefficients L_{ij}s ($i \neq j$) are not independent of proper coefficients L_{ii}s. This results in a simple form of the flux-ratio equation in terms of the ratio of partial molar volumes of diffusing components. Thus the parameter controlling the stability of the layer sequence in a reaction zone is not L-ratios but partial molar volume ratios. Because partial molar volume ratios have definite values at given temperature and pressure, only one layer sequence is stable.

Application

Consider an enstatite layer between forsterite and quartz at a given temperature and pressure. The layer is assumed to be polycrystalline with intergranular water. The entropy production σ by diffusion can be written as

$$T\sigma = J_{H2O}X_{H2O} + J_{MgO}X_{MgO} + J_{SiO2}X_{SiO2},$$

where T denotes temperature, J_i diffusive flux of i, and X_i stands for thermodynamic force conjugate to J_i. Variational principle for the steady state requires

$$\partial T\sigma /\partial X_{H2O} = 0. \qquad (eq.1)$$

Combining eq.1 and the Gibbs - Duhem relation for enstatite $X_{MgO} + X_{SiO2} = 0$ together with a volume – fixed reference frame:

$$V_{H2O}J_{H2O} + V_{MgO}J_{MgO} + V_{SiO2}J_{SiO2} = 0,$$

we get the following formula for the cross coefficients:

$$L_{MgOSiO2} = L_{SiO2MgO} = (V_{MgO}L_{MgOMgO} - V_{SiO2}L_{SiO2SiO2}) / (V_{MgO} - V_{SiO2}),$$

where V_i denotes a partial molar volume of diffusing species i. Finally we get the flux ratio equations:

$$J_{MgO} / J_{SiO2} = (L_{MgOMgO} - L_{MgOSiO2})/(L_{MgOSiO2} - L_{SiO2SiO2})$$
$$= - V_{SiO2}/V_{MgO} \equiv - \alpha$$

Using this relation, the total reaction can be written as

$(1+\alpha)$Quartz + $(1+\alpha)$Forsterite = $2(1+\alpha)$Enstatite.
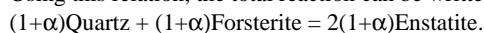
This paper also discuss an application to quartz - dolomite system, which is discussed by Joesten(1991), to show that Qtz/Talc/Talc+Calcite/Dolomite is an only possible layer sequence.

Selected Microbial Interactions with Actinide

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Microorganisms can interact with actinides by both direct interaction (biosorption, bioaccumulation, oxidation and reduction reactions) and indirect interaction (change of pH and redox potential). They may play an important role in the immobilization and mobilization of actinides in aquifers and subsurface environments.

This talk will present several detailed examples of the interaction of aerobic soil bacteria (Pseudomonas, Bacillus and Deinococcus strains) with uranium and plutonium. Details of the nature of the bacterial functional groups involved in the interfacial actinide interaction process will be reported. Based on time-resolved laser-induced fluorescence spectroscopy (TRLFS) and synchrotron X-ray absorption spectroscopy (XANES and EXAFS) studies, molecular-level mechanistic details of the different interaction processes will be discussed. Areas of this emerging field in actinide research will be outlined where additional information and integrated interdisciplinary research is required.

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