350e Diffusion in Polymeric Systems: Arrhenius and Free-Volume Equivalance

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Diffusion in polymeric systems have been described based on two approaches: One theoretical approach is based on the use of free volume during molecular migration and the other theory is based on the premise that a molecule must attain a certain activation energy before the diffusion or migration step can take place. In this work, we bridge these two basic approaches and show that they are related at the most basic theoretical level and information from one theoretical approach can be used to facilitate the use of alternative theoretical models. Being able to bridge the activation energy approach and the free-volume approach, offers the potential to utilize diffusion data for a few solvents diffusing in a given polymer with unknown free-volume characteristics to predict diffusion of other solvents in the same polymer. It is shown that the correlation of the activation energy and pre-exponential factor from the Arrhenius approach with solvent size can be used to obtain meaningful diffusion coefficients for trace amounts of a solvent diffusing in a polymer using information about solvent size alone. Experimental data for various polymer-solvent systems are used to test this approach.