## 267b Multicomponent Transport in Membranes: Theory and Experiment

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Coupled transport phenomena are well known in multicomponent systems. The presence of one component diffusing through a medium can be strongly influenced by the presence of another diffusing species. While these effects are generally recognized as important in membrane applications, few successful models have appeared that are capable of describing the coupling phenomena in a comprehensive fashion. Here we present a new theoretical approach to multicomponent diffusion in crosslinked polymers and confirming experimental studies. While motivated by our own work in pervaporation, the theory is generally applicable to other membrane systems.

We present a new model based on an underlying free-energy for the membrane phase; the free energy of mixing and of elastic deformation are included. Rigorous phase equilibrium calculations demonstrate the effects of the various molecularly controllable variables on equilibrium solubility; the effects of co-solvency and crosslinking density are clearly demonstrated. In addition, the availability of an underlying free-energy function allows the use of the chemical potentials directly as the driving force for diffusion within the framework of non-equilibrium thermodynamics. This provides a theoretically grounded treatment that explicitly yields the concentration dependence of the diffusion coefficients in an a priori manner. That is, both solubility and diffusivity are calculable based only on the crosslink density of the network and the interaction parameters between the components.

To predict fluxes, the concentration dependent diffusivities must be integrated over the compositional paths of both components through the membrane - a fact that appears not to be widely appreciated. The integration over the unknown path may be circumvented through Taylor series expansion about the an average composition within the membrane. Resulting analytical predictions for the permeate compositions are in agreement with observed behavior both in the literature and from our own laboratory. Pervaporation results for the benzene-cyclohexane system permeating through NBR membranes of varying degree of crosslinking are shown to be in excellent agreement with the new theoretical treatment.