

243e Finding Exact Separation Boundaries in Chemically Reacting Systems

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Residue curves and residue curve maps have been extensively studied for over 100 years, beginning with the work of Ostwald and Schreinemakers. For mixtures that have azeotropes separation boundaries may exist and these boundaries are important in separation process synthesis.

Much of the literature in this field deals with systems that do not react. However, over the last 20 years or so, reactive separations have attracted considerable attention. Chemical reactions can influence residue curve maps in some important ways. For example, reactions can lead to the disappearance of some azeotropes that exist in the absence of reaction. Chemical reactions can also lead to the creation of new azeotropes that would not exist in the absence of reaction. Even more intriguingly, it is possible for these so-called reactive azeotropes to exist even in systems that otherwise would be considered thermodynamically ideal. It follows that chemical reactions can influence the very existence of separation boundaries and, therefore, the design and synthesis of reactive separation processes.

Until recently there existed no precise (mathematical) definition of a distillation boundary. Recently, Lucia and Taylor showed that distillation boundaries for non-reacting ternary systems be characterized in terms of line integrals, surface areas for 4-component systems, volumes for 5-component systems, and so on. In particular, Lucia and Taylor show that separation boundaries for ternary azeotropic non-reacting liquid mixtures can be characterized as local maxima in the line integral from any unstable node to all reachable stable nodes. This property of separation boundaries allows us to devise an optimization method for the precise computation of these boundaries.

It is the purpose of this paper to show how the geometric approach described by Lucia and Taylor can be adapted for the rigorous determination of separation boundaries in reacting mixtures. Towards this end we provide a brief introduction to key concepts from the approach of Lucia and Taylor to defining and computing distillation boundaries in non-reacting systems. We then investigate residue curve maps for mixtures in chemical reaction equilibrium and in kinetically limited reacting mixtures. Numerical examples are shown to provide evidence in support of our approach.