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Moshe Gitterman: Chemistry Versus Physics: Chemical Reactions Near Critical Points

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Jim Baird

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In a book with the provocative title, "Chemistry Versus Physics: Chemical Reactions Near Critical Points," Professor Moshe Gitterman summarizes in 134 pages a number of theories and experiments which illustrate the coupling between critical phenomena and chemistry. By criticality in chemistry, we generally think of the slowing down in the net rate of reaction and the shift in the position of chemical equilibrium as the reacting mixture approaches a critical point. The solvent can be a pure fluid with a liquid-vapor critical point or a binary liquid mixture with a critical point of solution. In either case, the critical point of the solvent is generally different from that of the reaction mixture, which depends upon the concentrations of the reactants and products. To observe criticality in a reacting mixture, any change in temperature must catch up with the advancing or retreating critical temperature. If the chase is successful, the system is said to reach a critical end-point. Under ordinary laboratory conditions of fixed temperature and pressure, a strong critical effect in a reaction at the critical end-point of a binary liquid solvent is to be expected when the reactants and the solvent include no inert components.

After surveying the field in Chap. 1 "Criticality and Chemistry", in Chap. 2, titled "Effect of Criticality on Chemical Reaction," the author turns to the theory of critical slowing down of the net rate of reaction. Here he points out that there have been scattered, but persistent, experimental reports of both slowing down and speeding up. Invoking a mode coupling analysis that includes simultaneous rates of relaxation of fluctuations in density, extent of reaction, and entropy, he derives a system of coupled partial differential equations which describe the space-time kinetics of a reacting system near a critical point. By examining special cases, the author concludes that mode coupling theory can encompass both slowing down and speeding up.

In Chap. 3 "Effect of Chemistry on Critical Phenomena," the author describes the effect of a critical end-point on the heat capacity and the diffusion coefficient. In Chap. 4 "Phase Separation in Reactive Systems," he demonstrates how a reaction can force a system into a

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J. Baird (✉)
Department of Chemistry, University of Alabama in Huntsville, Huntsville, AL 35899, USA
e-mail: bairdj@email.uah.edu

phase transition when the conditions satisfy both the law of mass action and the chemical potential requirements for phase equilibrium. A partially ionized plasma with Debye-Huckel electrostatic screening serves as an example. As for the kinetics, if the reaction quenches the solvent into the meta-stable region, the theory of nucleation governs the rate of formation of the new phase, whereas if the reaction quenches the solvent into the unstable region, the theory of spinodal decomposition applies.

In Chap. 5 “Comments on the Geometry of the Phase Diagram of a Reaction Mixture,” the author discusses supercritical fluid solubility, azeotropic points, melting points, and double critical points. In Chap. 6 “Sound Propagation and Light Scattering in Chemically Reactive Systems,” mode coupling theory is again invoked. The final Chap. 7 “Conclusions” includes a description of the application of critical fluids to solvent extraction in chemical engineering.

“Chemistry Versus Physics” provides an excellent summary of the field of critical phenomena in chemistry and also offers *inter alia* many clues that could lead to future advances. I strongly recommend this book to physicists, physical chemists, and chemical engineers interested in critical phenomena.