Book Review: How Fluids Unmix

How Fluids Unmix: Discoveries by the School of Van der Waals and Kamerlingh Onnes. J. Levelt-Sengers, Koninklije Nederlandse Akademie van Wetenschappen, Amsterdam, 2002.

The author has provided us with a wonderful book. Mixed with the historical aspects of how the work of several Dutch scientists developed in the late nineteenth and early twentieth centuries the rather subtle questions relating to the thermodynamic behavior of fluids mixtures, a wealth of relevant technical aspects are included in the text, many of which are not often, if ever, mentioned in standard books on this subject.

The first three chapters of the book contain a summary of three of the main achievements of J. D. Van der Waals namely, his equation of state, the law of corresponding states and his theory of mixtures. Chapter 4 is particularly interesting as it places the reader in the situation that prevailed between 1873 and 1892. This is nicely done in pointing out the links between the work of Van der Waals, Helmholtz and Gibbs. At the same time the concepts necessary to appreciate the complicated behavior of mixtures are established.

Chapters 5 to 8 are, in my opinion, the core of this book. Here the very intrinsic nature of phase diagrams is explained in detail mainly in terms of the work of Korteweg, Kuenen, Kammerlingh Onnes, van Laar and Verschafellt. The material is splendid although not so easy to read. No detailed calculations are given, all the main arguments and results are expressed through diagrams taken from the original sources. Often these diagrams because of their inherent complexity are hard to follow. Trying to extract from them the relevant issues mentioned in the text is a question of patience and good eye-sight. Yet the reward is satisfying. Such material is not available almost anywhere else except a few articles or the original sources. The author has excelled herself in providing a very clear explanation of their content. One learns a lot about this subject by careful reading of this material.

Chapters 9–11 contain a clear account about criticallity and capillarity, subjects which although pioneered by Verschafellt in the nineteenth century, places the whole of phase transitions in the more modern language of critical exponents. Starting with the phenomenon of capillarity, which triggered this approach, the author also brings to the fore the old controversy about the persistence of the liquid phase and the experiments on phase separation of mixtures to the work on dilute near-critical mixtures incorporating here the contributions of van't Hoff and Keesom. The relevance of this work is emphasized in Chapter 11 leading to the today very relevant problem of supercritical fluids.

In the last Chapter (12), the overview of impact of the Dutch school to the whole subject of fluid mixture phase separation and fluid criticality is presented. In particular its impact on physical chemistry and some related topics developed in the Russian school is also dealt with. Finally, mention is made on the impact of all these ideas in the chemical process industry.

Undoubtedly this is a valuable contribution to the whole field of physical chemistry. By its reading one learns a great deal about many details that characterize the properties of fluid mixtures not available in standard sources. The presentation is not only clear but very carefully and logically written. I highly recommend its reading to all chemists, physical chemists and chemical engineers interested in the many aspects of phase separation.

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