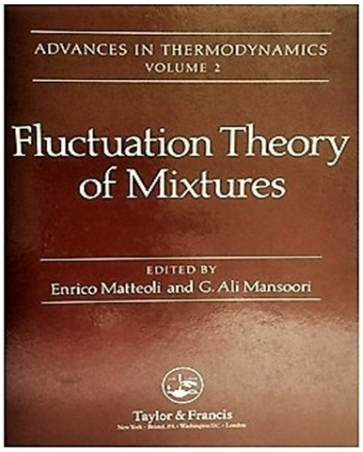


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# Fluctuation Theory of Mixtures

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# Introduction

In the last decade, after about a quarter of a century in which it has been almost ignored, the Fluctuation theory of mixtures, as developed by Kirkwood and Buff in 1951, has attracted the attention of more and more investigators, as demonstrated by the still increasing large number of papers recently published in international scientific magazines.

The topics treated in this literature range from the generalization and theoretical developments of the theory, to its applications in experimental physical chemistry and chemical engineering.

The applications which have been implemented are due to the recent theoretical developments which, on one hand, have allowed a more complete modelization of mixtures and consequently a better prediction and a more accurate calculation of thermodynamic quantities of mixtures, such as activity coefficients, partial molar volumes, solubility and phase behaviour in general; and, on the other, have promoted a deeper understanding of the microscopic structure of mixtures in terms of correlation functions, local composition, interfacial composition and size of clusters.

It is now certain that the theory is still susceptible of further important developments which will involve both its predictive potentiality as well as its capability in characterizing the local environment of molecules in mixtures. For this reason, we believe, the publication of a volume containing the state of the art of the fluctuation theory approach to mixtures will be welcome by all scientists who work in the general areas of basic and applied physical chemistry and of chemical process engineering.

To this purpose, as well as to draw attention to a topical research field which lends itself to interesting developments in different directions, we have here collected a series of articles written by investigators who have been and still are very active in this area.

After the first chapter, where the main conceptions and equations of statistical mechanics relevant to the subsequent articles are reviewed, three papers published in the fifties by Kirkwood and Buff, by Pearson and Rushbrooke, and by Mazo, respectively, are fully reproduced from the original magazines. These articles contain the fundamental equations and relationships among thermodynamic properties and correlation functions integrals of the fluctuation theory, and are therefore essential references for all chapters of the volume.

In O'Connell's paper, a new and more convenient formalism of the theory based on the integrals of the direct correlation functions is developed and used to obtain thermodynamic properties of pure and mixed liquids as well as of supercritical and ionizing substances in liquids.

mutual diffusion coefficient for binary non-electrolyte mixtures is obtained and the theory is shown to give a good qualitative and quantitative description of experimental behaviour.

The paper by Jonah presents a perturbation theory approach to the infinitely diluted solute chemical potential, with the solvent component as the reference. It deals mainly with the second order perturbation term, which is related to fluctuations. Applications to low-pressure vapour-liquid equilibria and solution thermodynamics, such as the calculation of Henry's constant and solid solubilities in supercritical fluids, are discussed.

In the last chapter, an extensive treatment of electrolyte solutions by means of the Kirkwood-Buff theory is presented by Newman. Starting from the theory equations for non-electrolyte solutions, new relations are derived for a variety of thermodynamic properties for solutions of salts which are conform to the ion-addivity rule and infinite dilution behaviour. The theory is used to interpret partial molal volumes, free energies of transfer and activity coefficients of electrolytes in solution.

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