

Thermodynamic Properties and Structure of Solutions

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The thermodynamic criterion of ideality gives only concentration dependences between the macro properties. In this connection, the question arises about the micro causes of the ideal behavior of the thermodynamic properties and the deviations from such dependence. I propose a structural description for perfect solutions, ideal and arithmetic ones based on statistical physics using such molecular descriptors as the packing density, the molecular size, and the intrinsic density. The influence of pure geometric factors (molecular size and shape) has been estimated on the thermodynamic properties such as the bulk density, the isothermal compressibility coefficient, and the thermal expansibility coefficient. This approach allows making quantity estimations of the mean microscopic parameters (molecular volume, packing coefficient, intrinsic density) for pure liquids based on the macro properties. The expression of the sound velocity for arithmetic solutions fits for mutual mixtures of close homologous hydrocarbons. Based on this approach the structural causes of convergence in the concentration dependences of excess properties for strongly non-ideal solutions are determined.