Equation of State of Liquids and Liquid Mixtures in Terms of Helmholtz Free Energy

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The use of free energy in the equation of state for liquid is especially interesting because it allows us to avoid the problem of the reference point in the integrals used to calculate calorical properties of thermal data. It has been shown that cellular model conceptions are applied for such equations of state, and the equation form depends on the selected potential of intermolecular interaction.

The theoretical bases of the equation include the following: liquid is represented as the ensemble of cells including molecules (one-particle filling), which interact with the cell by a selected potential; cells are independent and the energy of each cell is the microscopic Helmholtz free energy; the sum of the free energies of the cells is the free energy of the liquid system; the volume corresponding to one cell depends on both the average distance between particles and on packing parameters; the number of molecules forming the cell is equal to the coordination number. The introduced structural characteristics of liquids, the coordination number and packing parameter, depend on the temperature, but the form of this dependence is determined from the equation of thermodynamic properties at so-called ideal curves of the liquid thermodynamic surface. It has been shown, in particular, that the configuration part of the inner energy is a linear function of temperature on the ideal gas curve. In the resulting three-parameter equation of state with parameters which depend directly on the crystal properties, the form of the potential was obtained. This allows for the generalization of an equation for liquid mixtures for which known combination rules are applied.