Thermodynamic properties of coexisting phases of carbon tetrachloride on sublimation and melting lines

L.N. Yakub, **O.S. Bodiul**
Thermophysics Dept., Odessa National Academy of Food Technologies,
65039, Kanatnaya 112, Odessa, Ukraine
lydia.yakub@gmail.com

Methane CH_4, perfluoromethane CF_4 and carbon tetrachloride CCl_4 are the simplest representatives of a wide class of substances formed by molecules of tetrahedral symmetry. The increasing interest to these substances is due to the search for new energy-intensive molecular systems based on carbon materials suitable for storage and easy extraction of molecular hydrogen from them as fuel. CCl_4 (Freon R10) is one of the high-boiling substances. Its thermodynamic properties are well studied in the liquid phase and at the saturation line, but the amount of experimental data for the solid phase is limited.

The phase diagrams of methane, tetrafluoromethane, and carbon tetrachloride illustrate their complex structure and the presence of many high-pressure phases of these crystals. This work is devoted to study of the location of the melting line of CCl_4 on the phase diagram and to calculation of properties of coexisting phases of carbon tetrachloride at high pressure. We investigate the possibility of predicting the position of the melting line of carbon tetrachloride on the phase diagram, using separate equations of state for its solid and liquid phases in the framework of perturbation theory using a single small parameter;

In this study we consider exclusively phases I of solid CCl_4, which are characterized by relatively free rotation of molecules.

In the study of thermodynamic properties of carbon tetrachloride in the high-pressure region we used the equation of state previously developed for methane [1] in the framework of the thermodynamic perturbation theory and the potential model of intermolecular interaction, in which the Lennard-Jones potential was supplemented by non-central octopol-octopol interaction of methane molecules. The exact expression of the octopol-octupol interaction of methane molecules obtained in [1] was used for analytical representation.

The equation of state for a fluid was also constructed within the framework of thermodynamic perturbation theory, including the basic system (the Lennard-Jones fluid) and the perturbation correction. For the basic Lennard-Jones system the equation of state proposed by Kolafa and Nezbeda [2] was chosen, which gives the best description of computer simulation data for the Lennard-Jones fluid.

We discuss the limits of applicability of the equations of state of the solid and liquid phases proposed earlier for methane to calculate the thermodynamic properties of its halide derivatives.

Possibilities of application of the Monte Carlo computer simulation as a tool for studying the properties of condensed phases of CCl_4 in the region of extreme state parameters are discussed and computer simulations of crystalline CCl_4 in the fcc phase from $T = 245$ K to $T = 320$ K along the melting line were performed.

[1] Yakub L. N., Bodiul O. S. Melting Line Parameters and Thermodynamic Properties of Methane at High Pressures. Journal of Low Temperature Physics. 2017. Vol. 187. № 1. P. 33–42. DOI: 10.1007/s10909-016-1721-7
[2] Kolafa J., Nezbeda I. The Lennard-Jones fluid: an accurate analytic and theoretically-based equation of state. Fluid Phase Equilibria. 1994. Vol. 100. No. 1. DOI: 10.1016/0378-3812(94)80001-4