

Investigation of Essentially Different Energy Distributions of Molecular Orientations in Plastic Crystals

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A model of the energy states of molecules in plastic (orientationally disordered) crystals was presented in our previous papers [1,2]. According to that model, the existence of two types of molecular orientations is postulated for such crystals. There is a single 'basic' orientation (the lowest in energy) and n 'plastic' ones that are higher by $\Delta_{or}E$.

A number of other essentially different energy distributions of rotational orientations of molecules in plastic crystals are discussed in this paper. Mathematical expressions connecting the thermodynamic parameters of the 'ordered crystal to plastic crystal' transition with the number of non-equivalent orientations, n_{or} , and the energy difference between the 'basic' orientation and the energetically lowest 'plastic' one, $\Delta_{or}E$, were derived. A general function of energy distribution of molecular orientations was used here. The derived expressions were applied to five different distribution functions. The considered models of the energy states of molecules in plastic crystals were verified on the base of the experimental values of T_{trs} , $\Delta_{trs}S$ and $\Delta_{trs}C_p$ for a large group of organic compounds including halomethanes, hydrocarbons, derivatives of cyclohexane and adamantane. The thermodynamic parameters of phase transitions for some substituted adamantanes and cyclohexanes used in this analysis were obtained by the adiabatic and scanning calorimetry in our laboratory. The satisfactory quantitative agreement with experiment was achieved if the difference between neighboring $(k-1)^{th}$ and k^{th} energy levels of plastic orientations decreased as $\Delta E = 2^{1-k} \Delta_{or}E$ or $\Delta E = k^{-1} \Delta_{or}E$.

- [1] G.J. Kabo, A.V. Blokhin, M.B. Charapennikau, A.G. Kabo, and V.M. Sevruck, *Thermochimica Acta*, **345**, 125-133 (2000).
- [2] A.B. Bazyleva, A.V. Blokhin, G.J. Kabo, A.G. Kabo, and Y.U. Paulechka, *J. Chem. Thermodyn.* **37**, 643-657 (2005).