Determination of Thermodynamic Properties of Some Organic Compounds by Experimental and Calculation Methods for the Wide Temperature Range

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Fundamental basis for determination of the thermodynamic properties of individual organic compounds includes precise experimental methods of the phase equilibrium study and calculation methods based on the experimental data.

The liquid – gas equilibrium was investigated by 1) comparative ebulliometry for determination of the saturated vapor pressure in moderate temperature (293 K to 530 K) and pressure (2 kPa to 101 kPa) ranges and 2) adiabatic calorimetry for determination of the vaporization enthalpy at the room temperatures. Combined treatment of the vapor pressure and densities of liquids by corresponding states low in L.P.Filippov version allowed us to calculate the critical parameters T_c,V_c,and P_c. The low-temperature heat capacity measurements and solid phase transitions and fusion study were carried out by vacuum adiabatic calorimetry in the temperature range from 5 K to 373 K. Based on these data, changes of entropy, enthalpy, and Gibbs function have been computed for the condensed states in temperature range studied and for the ideal gas state at T = 298 K using enthalpy, entropy, and entropy of the ideal gas compression, obtained by ebulliometry and vaporization calorimetry. Molecular constants (vibrational frequencies, geometry, and potential functions of internal rotation) were computed at the B3LYP/6 density functional theory (DFT) level to obtain the ideal gas thermodynamic functions in wide temperature range from 100 K to 1500 K. Coincidence of the calorimetric and calculated values of the absolute entropy is considered as the reliability evidence of the all values used for the entropy calculations. Totality of the experimental and calculation data were used for reliable extending the vapor pressure of moderate interval to the whole range of liquid phase (from the triple to the critical temperatures) where the vapor pressure changed from some parts of a Pa to several MPa. The standard enthalpies of formation were obtained by DFT method using isodesmic reactions. This method was also applied for critical analysis and comparison of experimental literature data on the enthalpies of formation for some compounds that allowed us to reveal unreliable data and overestimate their uncertainties. In this paper, the thermodynamic data for some prospective compounds of different classes (alkyladamantanes, tertiary ethers, perfluorocarbons, and ferroce derivatives) will be presented.

This work was financially supported by the Russian Foundation for Basic Research (project № 05-02-17435).