

Comprehensive Study of Thermodynamic Properties for Cyclohexanone Oxime

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Cyclohexanone oxime (CHO) is an intermediate of the large-scale industrial synthesis of caprolactam. In our previous investigation of CHO [1] the sample purity was not characterized calorimetrically and there were discrepancies in the sublimation enthalpies determined calorimetrically and from vapor pressure measurements. Therefore, a new investigation of the thermodynamic properties of CHO has been carried out.

An industrial sample of CHO used in this study was purified by vacuum sublimation, and its purity was found to be 0.9998 from fractional-melting experiments. The heat capacities in the range of (5 to 370) K were measured with an adiabatic calorimeter. Two anomalies at (200 to 240) K and (260 to 300) K were found in the C_p - T curve for crystalline CHO. They correlate with the temperatures of the phase transitions for cyclohexanone ($T_{\text{trs}} = 220.8$ K, $T_{\text{fus}} = 245.2$ K) and cyclohexanol ($T_{\text{trs}} = 265$ K, $T_{\text{fus}} = 298$ K). The temperature ($T_{\text{fus}} = 362.20$ K) and enthalpy of fusion (12.45 ± 0.02) kJ/mol were determined. The thermodynamic properties of CHO in the condensed state were calculated from the experimental data.

The vapor pressure over crystalline CHO in the temperature range (291 to 323) K was obtained by the integral effusion Knudsen method. The vapor pressure over the crystalline (288 to 341) K and liquid (365 to 395) K compound was measured by the transpiration method. The thermodynamic parameters of vaporization and sublimation processes were calculated from the temperature dependences of the vapor pressure. The entropy of CHO in the gas state was evaluated from experimental data and calculated in a wide temperature range by the statistical thermodynamic method. Acknowledgements. This work was supported by the INTAS-Belarus foundation (grant № 03-50-5526)

[1] A.A. Kozyro, G.J. Kabo, V.S. Krouk et al, *J. Chem. Thermodynamics* **24**, 883 (1992).