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THERMODYNAMICS OF (THIO)AMIDES AND THEIR COMPOUNDS WITH MINERAL ACIDS AT (0-330)K

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ABSTRACT

Heat capacities for six (thio)amides and their inorganic acid compounds at (8-330)K and heats of combustion of three amides at 298.15K were measured in this work. Thermodynamic functions at (0-330)K and standard thermodynamic characteristics of formation at 298.15K for studied compounds were calculated.

INTRODUCTION

Amides and thioamides are widely used in various branches of national economy. Molecular complexes of acetamide and urea with acids are physiologically active and may be successfully used as plant growth regulators. However, thermodynamic properties of (thio)-amides and their compounds with acids are not well known.

MEASURING METHODS

Temperature dependences of heat capacity for acetamide (1), thiosemicarbazide (11), semicarbazide (111), urea nitrate (1V), acetamide nitrate (V), threeacetamide nitrate (V1) in (8-330)K were measured in adiabatic vacuum calorimeter (1). The apparatus and techniques used allow us to obtain heat capacity of substances in solid and liquid states with an error of about 0.5% at (10-50)K and 0.2% at (50-330)K and to measure the temperatures of physical transitions with an error up too 0.01K.

The heat of amide combustion at 298.15K (2) was determined in isothermal calorimeter V-08M with a static bomb. The energy calorimeter equivalent was determined by standard benzoic acid K-2. The apparatus was tested by determination of $\Delta_c H^\circ$ standard amber acid.

The purities of studied compounds were found to be 99.76 mass % for (1), 99.84 for (11), 99.83 for (111), not less than 99.73, 99.75, 99.74 for (1V), (V) and (V1) respectively, 99.80 for

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benzamide (V11).

RESULTS AND DISCUSSION

Heat capacity and characteristics of physical transition.

C_p^o of (1) and (1V) has been studied at (13-330)K, (11) at (8-330) K,(111),(V) and (V1) at (60-330)K.Experimental C_p^o values and average C_p^o=f(T) curves are shown in figure.

Temperature dependences of heat capacity of (1),(111)-(V1) gradually increase as the temperature rises with no peculiarities observed in (1),(111) and (1V).Anomalous of heat capacity increase of (V) and (V1) in > 280K region can be connected with the begining of complex melting: T_m=361 and 337K respectively.

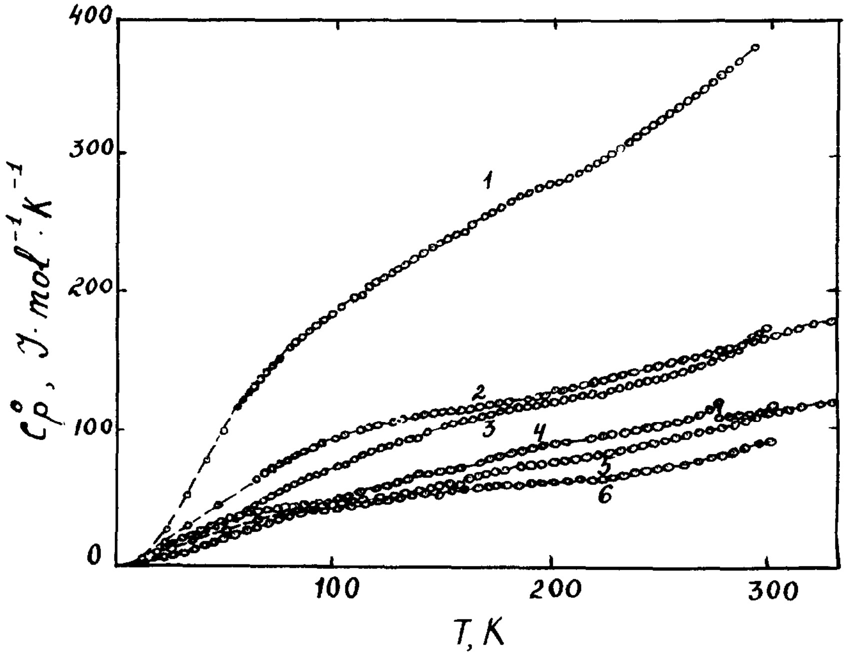

Fig.Heat capacity of threeacetamide-2, nitrate-1,acetamide nitrate-2, urea nitrate-3,thiosemicarbazide-4, semicarbazide-5,acetamide-6.

The heat capacity curve of (ll) at (260-270)K shows a gradual comparatively quick increase of C_p^o and its sharp decrease at the temperature corresponding to the upper level of the region. Such dependence of C_p^o vs.T is usually connected with physical transformations of crystals (3)which belong to the so-called "order$\rightleftarrows$disorder" type λ-transitions due to the form of $C_p^o=f(T)$ in transformation range.Accoding to our calorimetric data transition thermodynamic characteristics of (ll)are:$T_{tr}=(268.9\pm0.1)$ K; $\Delta_{tr}H=(70.0\pm0.7)J\cdot mol^{-1}$; $\Delta_{tr}S=(0.250\pm0.002)J\cdot mol^{-1}\cdot K^{-1}$.

Physical nature of studied transformation of thiosemicarbazide is apparently the same as for thiourea (4) caused by its ferroelectrical properties.

Thermodynamic functions.To estimate the thermodynamic functions of (l)-(Vl) at (0-330)K C_p^o were extrapolated to 0°K according to Deby's heat capacity function C_p^o= nD(Θ/T) and to Kelley-Parks-Huffman's method (5)for (l),(ll),(lV) and (lll),(V),(Vl) respectively.The functions values at 298.15K and p=101.325kPa are C_p^o=91.27 $J\cdot mol^{-1}K^{-1}$,$H^o-H^o(0)$=16.01 $kJ\cdot mol^{-1}$,S^o=115.0$J\cdot mol^{-1}\cdot K^{-1}$, - $G^o-H^o(0)$ =18.29 $kJ\cdot mol^{-1}$(l); 114.3, 19.12, 128.2, 19.10 (ll); 110.6, 18.12, 119.6, 17.53 (lll); 158.6, 27.49, 189.2, 28.97(lV); 175.0, 29.93, 210.5, 32.78(V);383.0, 64.43, 443.8, 67.90 (Vl).

The heats of combustion at 298.15K and $p=3\cdot10^3$kPa are measured and standard enthalpies of formation are calculated for (l),(lll) and benzamide(Vll).Values Δ_cH^o and Δ_fH^o are respectively equal -1186.03±0.82 and -315.60±0.82 $kJ\cdot mol^{-1}$(l), -882.40±0.60 and -225.68±0.60 $kJ\cdot mol^{-1}$(lll), -3546.54±1.87 and -208.53±1.87 $kJ\cdot mol^{-1}$ (Vll).

Standard thermodynamic characteristics of formation for(l), (lll) and (Vll) are given in Table.

Table

Thermodynamic characteristics of formation for crystalline acetamide,semicarbazide and benzamide, T=298.15K,p=101.325 kPa

compound	$-\Delta_fH^o$ $kJ\cdot mol^{-1}$	$-\Delta_fS^o$ $J\cdot mol^{-1}\cdot K^{-1}$	$-\Delta_fG^o$ $kJ\cdot mol^{-1}$
CH_3CONH_2	315.60	421.05	190.06
$NH_2NH\ CONH_2$	225.68	602.20	46.14
$C_6H_5CONH_2$	208.53		

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