EXPERIMENTAL INVESTIGATION OF THE ISOBARIC HEAT CAPACITY AND THERMAL CONDUCTIVITY OF N_2O_4—NO SOLUTIONS IN THE LIQUID PHASE

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We discuss the results of the experimental investigation of the isobaric heat capacity and thermal conductivity of liquid N_2O_4—NO solutions with an NO concentration up to 0.08 parts by weight.

At the Nuclear Power Institute of the Academy of Sciences of the Belorussian SSR a great deal of attention is being given to the study of the thermodynamic and transfer properties of equilibrium-dissociating nitrogen tetroxide and mixtures based on it in the liquid and gaseous phases. Reliable data on the heat capacity and thermal conductivity of N_2O_4—NO solutions can be obtained only by direct experimentation, owing to the highly nonideal nature of such mixtures and the large contribution made by the reaction components to these properties.

Heat Capacity. We know of two studies devoted to the experimental investigation of the isobaric heat capacity of the nitrogen tetroxide in the liquid phase at atmospheric pressure [1,2]. The difference between the results of these studies amounts to 2.5% at 287°K, which considerably increases the estimates of the errors made by the authors. The isobaric heat capacity of liquid N_2O_4—NO solutions has not been experimentally studied up to now.

The heat capacity C_p of solutions was studied in the 280-305°K range and at pressures from 1.4 to 2.1 bar by the method of stationary flow-through calorimetry in a closed circulation scheme. The hermetically sealed apparatus has been described in detail in [3]. For the first time in such experiments, the flow rate was measured by the method of dynamic suspension using comparator weights (see, e.g., [4]) permanently included in the circulation loop. The design of the weight apparatus made it possible to make discrete measurements of the flow rate (5-6 times) during the time of the C_p measurements (15-20 min) for one calorimetric experiment.

The flow rate of the liquid under investigation was calculated by the following formula [3]:

$$G=\gamma\,\frac{M-(dm/dp)\,\Delta p}{\tau}\,m_a.$$

Here γ is a coefficient related to the dynamic nature of the flow-rate measurements and determined in special calibrating experiments; $\gamma = 1.0216$; M, mass of one calibration load, g; dm/dp, sensitivity of the comparator weights to a change in pressure in the apparatus during the measurement time, g/bar; Δp, τ, respectively, the average values of the variation in pressure in the apparatus and the interval of time between two instants of equilibrium of the comparator weights during the flow-rate measurement time, in bar and seconds; m_a, a coefficient taking account of the aerostatic force.

The coefficient m_a was determined from the formula

$$m_a=(1-\rho_a/\rho_l)/(1-\rho''/\rho'),$$

where ρ_a, ρ_l, ρ'', ρ' are, respectively, the densities of the air, the calibration load, the vapor, and the liquid in the measuring volume of the weight apparatus. To calculate m_a, we used pvTx data from [5]. The value of m_a in the experiments was found to range from 1.00242 to 1.00380, depending on the density and composition of the solution being investigated on the boiling curve.

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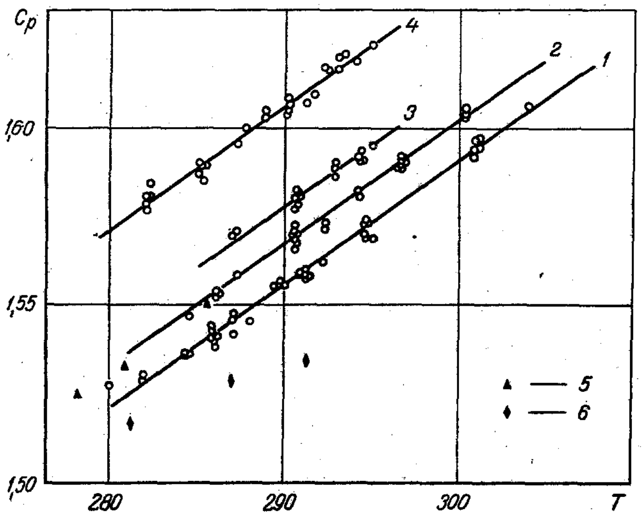

Fig. 1. Experimental C_p data: 1) $x_{NO} = 0$; 2) 0.112; 3) 0.0207; 4) 0.0491 wt. by parts; 5) C_p [1]; 6) C_p [2]. C_p, kJ/kg·deg K; T, °K.

The value of dm/dp was determined in special calibrating experiments and found to be $0.91 \cdot 10^2$ g/bar. Since the change in pressure in the apparatus during one discrete measurement of the flow rate did not exceed $\pm 1.0 \cdot 10^{-3}$ bar, the correction $(dm/dp)\Delta p$ was no more than 0.03% of the flow rate. The flow rate of the substance in the experiments was found to be between 1.9 and 2.6 g/sec. The systematic error of the flow-rate measurement was 0.08% with a confidence probability of 0.95.

In our study we used a widely known type of flow-through calorimeter [6] with no essential design changes. The temperature drop in the calorimeter was measured by two PTS-10 platinum resistance thermometers connected in series in the power input circuit. The main calorimetric experiment was necessarily preceded by an experiment in which the calorimetric heater was disconnected. The value of the heat exchange between the calorimeter and the environment, not exceeding 0.2% of the heater power in the experiments, was taken into account by means of a heat meter — a multijunction differential thermocouple.

The heat-meter sensitivity k was determined systematically as the experiment progressed in paired experiments with identical flow rate G and identical calorimeter temperature. When the heater was disconnected, large heat fluxes opposite in direction passed through the heat meter. Under these conditions the sensitivity of the heat meter is given by

$$k = dq/d\varepsilon = C_p G\,(\Delta t_I^0 - \Delta t_{II}^0)/(\varepsilon_I^0 - \varepsilon_{II}^0),$$

where for the experiments under consideration (I and II) Δt_I^0, Δt_{II}^0 are the temperature drops in the calorimeter, in deg; ε_I^0, ε_{II}^0 are the heat-meter readings, in mV.

Because experiments I and II were close to each other in time, it was possible to obtain a reliable determination of the quantity $(\Delta t_I^0 - \Delta t_{II}^0)$. The sensitivity was measured in experiments with water and with nitrogen tetroxide; it amounted to 0.043 W/mV for a determination error of no more than 10%.

The isobaric heat capacity was calculated on the basis of the values measured in the experiment and averaged according to the equation

$$C_p = \frac{N + k(\varepsilon - \varepsilon_0)}{\Delta t - \Delta t_0}\,G^{-1},$$

where N is the power of the calorimetric heater, in W; ε, ε_0 and Δt, Δt_0, respectively, are the heat-meter readings and the temperature drops in the main experiment and in the experiment with disconnected heater, in mV and in deg.

The temperature of the substance under investigation at the calorimeter input was kept constant to within $(3\text{-}5) \cdot 10^{-3}$ deg.

In the investigation we used N_2O_4–NO solutions with a nitric oxide concentration of $x_{NO} = 0.0000$; 0.0112; 0.0207; 0.0491 parts by weight. The concentration of hydrogen-bearing

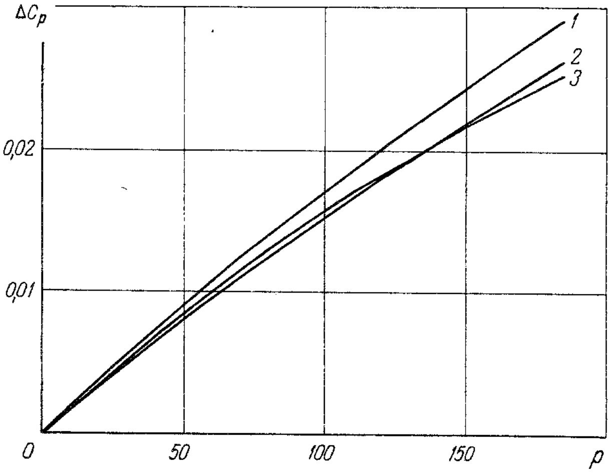

Fig. 2. Results of the calculations of ΔC_p: 1) ΔC_p [10]; 2) present study 3) ΔC_p [8]; ΔC_p, kJ/kg·deg K; p, bar.

impurities, recomputed to HNO_3, did not exceed 0.002 parts by weight. The composition of the solution was determined by analyzing specimens of the substance under investigation using the methods of gas chromatography and dielcometry [7]. The specimens were taken at the calorimeter input. The error in the analysis was estimated at 7%.

The 110 experimental values of the heat capacity of the solutions were fitted by a single equation using the least-squares method:

$$C_{p=1}0.5465+1.026\,x_{NO}+0.00348\,T\ (\mathrm{kJ/kg\cdot deg}). \qquad (1)$$

The mean-square deviation of the experimental data from the data calculated by Eq. (1) was 0.0024 kJ/kg·deg with a probability of 0.95. The limiting relative error of the data was estimated at 0.16% for $x_{NO} = 0.0000$ parts by weight and increases by about 0.05% for each 0.01 part of NO by weight. The results of the investigation are shown in Fig. 1.

The maximum deviation of the data obtained, $\delta = (C_p[\ ] - C_p)100\%/C_p$, from the results of [1,2] amounted to +0.7 and −1.6%, respectively. In our view, the data of the present study are preferable.

In order to determine the heat capacity of N_2O_4–NO solutions at high pressures from the data of [5], we calculated the quantity

$$\Delta C_p = T\int\limits_{p=1}^{p} (\partial^2 v/\partial T^2)_{p,x_{NO}}dp$$

for temperatures of 275-310°K, pressures of 1-250 bar, and nitric oxide concentrations of $x_{NO} = 0.05$–0.25 parts by weight. We obtained the following empirical relation:

$$\Delta C_p\cdot 10^6 = T\left[\sum_{i=0}^{3}(a_i+b_i\Theta)\,\pi^i + x_{NO}\sum_{i=0}^{3}(c_i+d_i\Theta)\,\pi^i\right] \qquad (2)$$

with the coefficients

$$a_0 = 2.06,\ b_0 = -0.93,\ c_0 = 8.8,\ d_0 = -3.2;$$
$$a_1 = -206.54,\ b_1 = 92.8,\ c_1 = -884.5,\ d_1 = 316.0;$$
$$a_2 = 53.4,\ b_2 = -21.1,\ c_2 = 157.6,\ d_2 = -51.5;$$
$$a_3 = -9.89,\ b_3 = 3.64,\ c_3 = -1.977,\ d_3 = 0,$$

where $\Theta = T/100$; $\pi = p/100$.

The relative error ΔC_p of the determination does not exceed 10%. The weak linear relation between ΔC_p and x_{NO} enabled us to extrapolate Eq. (2) reliably to $x_{NO} = 0$. The values of ΔC_p obtained are in good agreement with the values of ΔC_p given in [8], determined from

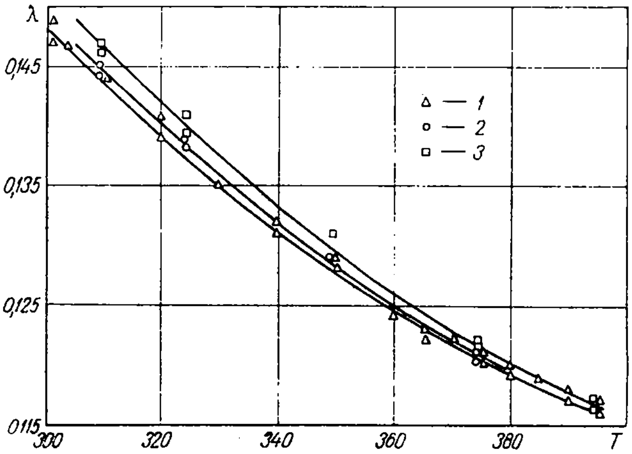

Fig. 3. Data on thermal conductivity: 1) x_{NO} = 0.0; 2) 0.04; 3) 0.08 wt. by parts. λ, W/m·deg K.

the data of [9] (Fig. 2). The divergences from the results of [10] are larger and lie in the 8-12% range.

Thermal Conductivity. On our new working segment, using the relative method of coaxial cylinders, we performed an experimental determination of the thermal conductivity of an N_2O_4–NO solution in the liquid phase for parameters in the 320-400°K and 20-160 bar ranges, for NO concentrations of 0.04 and 0.08 parts by weight.

In calibrating the working segment in the investigated range of parameters, we used helium and argon. Using 100 calibration points, we found the coefficients of the working formula in [11]. The mean-square deviation of the calibration points from the tabulated points for helium and argon [12] amounted to no more than 2% with a confidence of 0.95.

The thermal conductivity of N_2O_4–NO solutions was studied at pressures of 20, 50, 80, 120, and 160 bar on the 320-400°K isotherms with a step of 10°. The nitric oxide concentration was determined by the gas-chromatography method on each isotherm before and after the experiments. On this same working segment we found more precise values for the experimental data of [13] on the basis of the thermal conductivity of pure nitrogen tetroxide in the liquid phase.

An analysis of the results obtained shows that the addition of nitric oxide increases the thermal conductivity of an N_2O_4–NO solution over that of pure N_2O_4. This increase amounts to $\sim 0.3 \cdot 10^{-2}$ W/m·deg for an NO concentration of up to 0.09 parts by weight.

All the experimental points relating to the thermal conductivity of the N_2O_4–NO solution lie systematically above the corresponding points for pure N_2O_4. In Fig. 3 we show the experimental points and graphically smoothed curves for the thermal conductivities of pure N_2O_4 and N_2O_4–NO solutions with NO concentrations of 0.04 and 0.08 parts by weight on the 50-bar isobar. It can be seen that as the temperature increases to 380-390°K, the thermal conductivities of the N_2O_4–NO solution and the pure N_2O_4 coincide. This behavior can, in our opinion, be explained by the existence of an N_2O_4–N_2O_3–NO_2–NO system in the liquid phase and in the dense gaseous state. To calculate theoretically the composition of such a system is a very difficult problem at present. It is therefore of practical interest to set up an empirical formula of the type $\Delta\lambda = f(p, T, x_{NO})$ on the basis of the experimental material obtained.

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EXPERIMENTAL STUDY OF THE DENSITY OF ALIPHATIC ALCOHOLS AT VARIOUS TEMPERATURES AND PRESSURES

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Using a hydrostatic suspension method, the densities of ethyl, n-propyl, isopropyl, n-butyl, and isobutyl alcohols were measured in the temperature range 200-570°K and in the pressure range 10.86-491.4 bar.

The density of aliphatic alcohols in the liquid state were previously investigated mostly at atmospheric pressure and at the saturation line. At higher pressure measurements were carried out by a number of authors [1-5] in a quite wide range of state parameters with an error of 0.4-0.5%.

A device using the method of hydrostatic suspension was designed with the purpose of obtaining more accurate p, V, T data for alcohols. It differed from those used earlier [6] by more refined device construction, providing reliable operation at high temperatures and pressures, using more accurate measurement techniques and new electronic components, simpler and more convenient to use.

A correction was included in the calculation, including the effect of an external magnetic field on the power coil.

The pressure was created and measured by means of class 0.05 MP-60 and MP-600, and the

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