SPECIFIC HEAT OF AQUEOUS HNO_3 SOLUTIONS AT LOW TEMPERATURES (DOWN TO − 196°C)

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An experimental method is shown by which the specific heat of aqueous HNO_3 solutions has been determined at low temperatures.

Visual observations of $HNO_3-H_2O-N_2O_4$ solutions have revealed that at low temperatures there exist two forms of "ice" and one transition state, all of which were characterized in [1] as anomalies. This study here is concerned with the specific heat of aqueous HNO_3 solutions (25, 50, 78%) as well as of pure water and pure acid.

Experiments with various concentrations have yielded a relation between the specific heat and the relative content of both components and the temperature, making it possible to plot $c = f(T)$ curves for those various solutions.

Nowadays the specific heat is most often measured by the adiabatic calorimeter method, with the measurable heat supplied either periodically or continuously. The latter mode was selected for this particular case, the test time being here much shorter than with periodic heating.

The said method provides for heating a container with the test substance by a constant thermal flux. From the temperature thermogram one can determine the specific heat of the substance as a function of the temperature (Fig. 1).

A comparison of various container shapes has revealed the advantages of a cylindrical cell hermetically covered, with a heater and a thermometer at the surface. A cylindrical shape is convenient for ensuring adiabaticity and for determining, analytically and rather simply, the temperature distribution as well as the mean-over-the-volume temperature during heating of that cell [2].

The formula for calculating the specific heat c at temperature T is [2]

$$c = \frac{P - C_c b}{mb}, \tag{1}$$

with $b = dT_V/d\tau$ denoting the rate of change of the mean-over-the-volume temperature in the test substance.

During quasisteady heating of a specimen the rates of change of the surface temperature T and of the mean-over-the-volume temperature T_V are both equal:

$$\frac{dT}{d\tau} = \frac{dT_V}{d\tau} = b. \tag{2}$$

The thermal capacity of the test cell proper C_c is determined according to the formula

$$C_c = \frac{P}{b}. \tag{3}$$

The apparatus is shown schematically in Fig. 2. The adiabatic housing around the test cell is 180 mm high and 85 mm in diameter, with a removable top part. The test cell, 140 mm high and 35 mm in diameter, fits in a thin-walled shell which is suspended inside the adiabatic housing and held in place with

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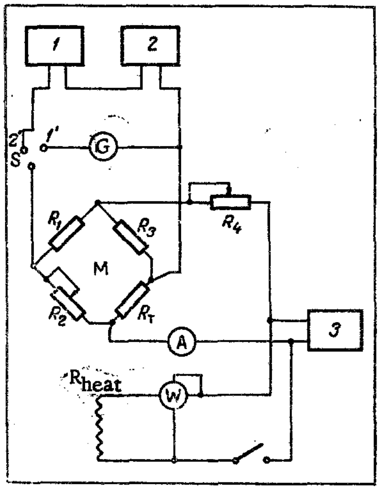

Fig. 1

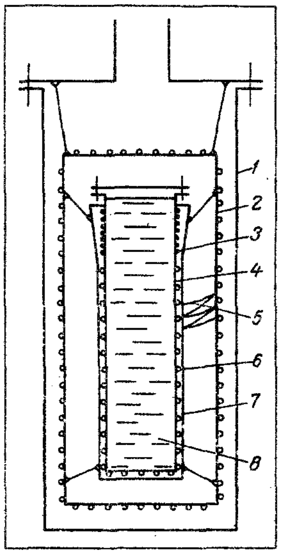

Fig. 2

Fig. 1. Electric circuit for measuring and recording the temperature of the test cell: 1) low-resistance potentiometer; 2) automatically operating electronic potentiometer; 3) dc voltage stabilizer.

Fig. 2. Apparatus for adiabatic heating: 1) low-temperature vacuum vessel; 2) adiabatic housing; 3) resistance thermometer for measuring the test cell temperature; 4) heater for the adiabatic housing; 5) three differential thermocouples; 6) heater for the test cell; 7) shell (case) for the test cell; 8) test cell with the tested substance.

Nichrome wires. Three differential thermocouples for measuring the temperature difference between housing and cell have been cemented to the respective surfaces. The thermal emfs of the differential thermocouples are fed to the input of a highly sensitive dc amplifier (model F 116/2). The amplifier signal is then fed first to a voltage amplifier (model UIPP-2) and from there to a power amplifier. The heater for the adiabatic housing is connected to the output of that power amplifier supplying its maximum 75 W to a 200 Ω (heater resistance) load.

The system for controlling the temperature of the adiabatic housing, with the test cell temperature as the reference, is continually driving the difference between these two temperatures to a minimum and this minimum is in turn defined by the gains of the three amplifiers. The difference between these two temperatures does not exceed 1°C.

The test cell temperature is measured and recorded by means of a bridge circuit M (Fig. 1) with the resistance thermometer R_T in one arm.

The bridge circuit M shown here represents one variant of connecting four conductors and allows for a proper compensation of the resistances of leads, inasmuch as these become of the same order of magnitude as resistance R_T at the boiling point of nitrogen ($R_T = 4.37\ \Omega$, $t = -196°C$).

Resistance R_T is determined from the ratio of bridge arms during balance:

$$R_T = \frac{R_2 R_3}{R_1}.$$

Here $R_1 = 10{,}000\ \Omega$ and $R_3 = 2000\ \Omega$. Resistances R_1 and R_3 should be much higher than R_2 and R_T. They are selected to meet the requirement that the measuring current in the bridge must not vary by more than ±0.5% as the resistance changes from its value at room temperature to its value at the nitrogen boiling point.

The bridge is balanced by reducing the deflection of galvanometer G to zero.

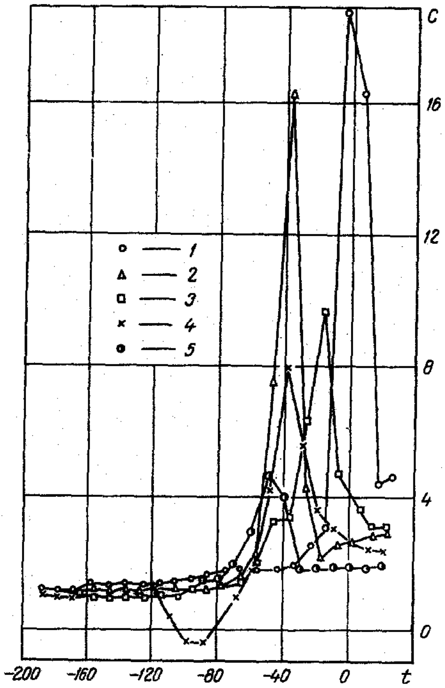

Fig. 3. Specific heat C (kg/kg · deg) of aqueous HNO_3 solutions as a function of the temperature t (°C), from −196 to +20°C, for: 1) pure water; 2) 25% HNO_3; 3) 50% HNO_3; 4) 78% HNO_3; 5) 100% HNO_3.

The temperature, proportional to the bridge M unbalance voltage, is recorded automatically through an electronic potentiometer 2 (model ÉPP-09M3) with 10 mV divisions on the scale. The measuring current in the bridge circuit was selected so that 1 mV on the scale corresponded to a 1°C change in the thermometer reading R_T. Voltages above 10 mV are recorded through a low-resistance potentiometer 1 as the voltage source with a polarity opposite to that of the bridge unbalance voltage. The systematic error of data recorded over the 60-70°C temperature range can be determined during bridge balance and then eliminated by an adjustment of the measuring current.

The heater power for the test cell is measured with a wattmeter W. The heater and the bridge circuit are energized from a common stabilized dc voltage supply (model P136) 3. A more thorough description of the apparatus can be found in [3].

The test procedure was as follows. First of all, the thermal capacity of the test cell proper was determined from a heating thermogram with the cell empty. From a heating thermogram taken with the test substance filling this cell, the specific heat of that substance was determined according to formula (1).

The thermal capacity was determined as follows. The test cell was placed in the adiabatic housing, which in turn was mounted through four thin wires to the flange of a low-temperature vacuum vessel (Fig. 2) and cooled with liquid nitrogen down to the nitrogen boiling point. The cup of that low-temperature vessel was bolted to the cooled test cell and its adiabatic housing on top, both hermetically held together at the flanges. The vessel was also immersed in a Dewar flask with liquid nitrogen and a vacuum (0.1 mm Hg) was maintained inside. The system of amplifiers for controlling the temperature of the adiabatic housing with reference to the test cell temperature was switched on during a test. After the amplifier tubes had warmed up, the test cell continued to be heated adiabatically.

The initial temperature of the cooled test cell was determined from the value of resistance R_T during bridge M balance (Fig. 1). The measuring diagonal of the bridge circuit was connected to potentiometer 2 by throwing switch S from position 1' ("balance the bridge") to position 2' ("record the temperature"). This in turn actuated potentiometer 2 and applied a voltage to the test cell heater. The heater power was here 3 W.

The thermal capacity was determined as an average over each 10°C interval.

The weight of a test specimen was ~190 g, measured accurately within 0.01 g.

The composition of a substance was checked before and after the experiment. It was found to have remained constant, within 1.5%, throughout.

The absolute error ε in determining the specific heat did not exceed [2]

$$\varepsilon = 0.03c + 0.06.$$

The test results have yielded a relation between specific heat and temperature (Fig. 3) for aqueous HNO_3 solutions and have revealed the existence of a negative specific heat in the case of a 78% HNO_3 solution. This negative value of specific heat is obtained by differentiating the thermodynamic equation of enthalpy

$$\sum_\alpha dH^\alpha = \sum_\alpha dQ^\alpha + \sum_\alpha V^\alpha\, dp + \sum_\alpha \sum_i \mu_i^\alpha dm_i^\alpha, \tag{4}$$

where superscript α refers to the phase and subscript i refers to the i-th component.

The system is here in a nonequilibrium state (self-heating). The preceding equation remains valid also for nonequilibrium states, if the rate of the respective process in "not too fast" [4]. In our case the given phase is almost homogeneous at every instant of time. The extreme conditions of turbulent flow or very high temperature and pressure gradients must be excluded from consideration.

Resolving expression (4) and considering that the system is characterized by parameters T and p, we have

$$\begin{aligned}\sum_\alpha T dS^\alpha = {} & \sum_\alpha \left(\frac{\partial H^\alpha}{\partial T}\right)_{p,m_i^\alpha} dT + \sum_\alpha \left(\frac{\partial H^\alpha}{\partial p}\right)_{T,m_i^\alpha} dp \\ & + \sum_\alpha \sum_i \left(\frac{\partial H^\alpha}{\partial m_i^\alpha}\right)_{T,p} dm_i^\alpha - \sum_\alpha V^\alpha dp - \sum_\alpha \sum_i \mu_i^\alpha dm_i^\alpha.\end{aligned} \tag{5}$$

Knowing that the composition of both phases is constant, we substitute $\partial H^\alpha / \partial x_i^\alpha = \mu^\alpha$ in (5):

$$\frac{\partial H^\alpha}{\partial p} = \frac{\partial}{\partial p}(G^\alpha - TS^\alpha) = \frac{\partial}{\partial p}\left[G^\alpha - T\left(\frac{\partial G^\alpha}{\partial T}\right)_{p,m_i^\alpha}\right] = V^\alpha - T\left(\frac{\partial V^\alpha}{\partial T}\right)_{p,m_i^\alpha},$$

and obtain

$$\sum_\alpha T dS^\alpha = \sum_\alpha \left(\frac{\partial H^\alpha}{\partial T}\right)_{p,m_i^\alpha} dT - \sum_\alpha T\left(\frac{\partial V^\alpha}{\partial T}\right)_{p,m_i^\alpha} dp. \tag{6}$$

The last expression yields the specific heat of the heterogeneous system

$$C_p = \sum_\alpha C_p^\alpha - \sum_\alpha T\left(\frac{\partial V^\alpha}{\partial T}\right)_p \frac{dp}{dT}. \tag{7}$$

A 78% HNO_3 solution in water is a two-component system. For the coexisting phases we have

$$C_p = C_p^{(1)} + C_p^{(2)} - (V^{(1)}\beta^{(1)} + V^{(2)}\beta^{(2)})\frac{\Delta H}{\Delta V}, \tag{8}$$

where superscripts 1 and 2 refer to phase 1 and phase 2, respectively,

$$\left(\frac{\partial V}{\partial T}\right)_p = \beta V, \quad \frac{dp}{dT} = \frac{1}{T}\frac{\Delta H}{\Delta V},$$

with ΔH and ΔV denoting the increments of enthalpy and volume during phase transition.

The expressions for ΔH and ΔV in a heterogeneous system will not be analyzed here.

The subcooled phase 2 passes into phase 1 in this particular case. If the heat of phase 2–1 transition is greater than the heat expended on heating these phases, then self-heating will occur. The total heat capacity of system (8) becomes negative.

The thermal capacity of a heterogeneous system depends on the value of the last term in (8).

NOTATION

c is the specific heat;
P is the power supplied to the heater;

T	is the temperature;
T_V	is the mean-over-the-volume temperature;
m	is the mass;
τ	is the time;
C_c	is the thermal capacity of the test cell;
R_T	is the thermometer resistance;
ε	is the absolute error in determining the specific heat;
H	is the enthalpy;
Q	is the quantity of heat;
V	is the volume;
p	is the pressure;
μ_i	is the chemical potential of the i-th component;
m_i	is the mass of the i-th component;
G	is the Gibbs thermodynamic potential;
S	is the entropy;
β	is the thermal expansivity;
C	is the thermal capacity.

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