EXPERIMENTAL INVESTIGATION OF THE ENTHALPY OF THE CHEMICALLY REACTING SYSTEM $\mathrm{N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2}$

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Abstract

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Corresponding Member of the USSR Academy of Sciences A. E. SHEINDLIN, N. I. GORBUNOVA, Yu. A. SARUMOV

EXPERIMENTAL INVESTIGATION OF THE ENTHALPY OF THE CHEMICALLY REACTING SYSTEM $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$

At the present time interest is increasingly growing in the study of the thermophysical properties of chemically reacting systems, in particular, dissociating nitrogen tetroxide,

$$N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2.$$

In recent years numerous works have appeared in which an attempt has been made at a theoretical description of the thermophysical properties of nitrogen tetroxide, for example ([1,2]). In addition, there are a number of experimental investigations of the properties of N_2O_4 ([3–7]). However, the available experimental data on the thermophysical properties of N_2O_4 do not make it possible to give a reliable theoretical description of the thermodynamic surface of state; this applies especially to the caloric properties, knowledge of which is of the greatest interest owing to the very substantial thermal effect of the chemical reaction.

In the present work, for the first time, the enthalpy of nitrogen tetroxide in the liquid phase has been studied in detail by experiment, and new data have been obtained on the enthalpy at supercritical temperature. The experiment was carried out at pressures from 50 to 300 kg/cm^2.

Fig. 1. Schematic of the experimental setup for determining enthalpy: **1**—sealless pump with electromagnetic drive; **2**—calorimetric flowmeter; **3**—enthalpy calorimeter, where the substance under investigation is heated to the required temperature and the calorimetric experiment for determining enthalpy is carried out; **4**—refrigerator; **5**—thermostats for maintaining constant temperature at the inlet to the calorimeters.

To determine the enthalpy of N_2O_4, the method of direct heating of the substance under investigation in a flow arrangement was used ([8,9]). The essence of the method is as follows. To the substance under investigation, circulating by means of pump **1** (Fig. 1) in the loop of the experimental setup at high

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pressure P with flow rate G, measured in the calorimeter-flowmeter **2**, as it passes through the enthalpy calorimeter **3**, heat Q is supplied from an electric heater. As a result, the substance is heated from temperature T_{in} at the inlet to the enthalpy calorimeter to temperature T at the outlet. Since the heat input is carried out isobarically (the hydraulic resistance of the enthalpy calorimeter is very small), the increment of the enthalpy of the substance $\Delta i(p, T - T_{\text{in}})$ in the temperature interval from T_{in} to T can be determined from the relation

$$\Delta i(p, T - T_{\text{in}}) = (Q - \Sigma Q_{\text{loss}})/G, \tag{1}$$

where ΣQ_{loss} is the total magnitude of the heat losses in the calorimetric experiment.

Measurement of the temperatures T_{in} and T was carried out with standard platinum resistance thermometers by the potentiometric method, using a P-308 potentiometer, and the pressure was measured with a standard piston manometer MP-600. The heat losses in the experiment were determined by means of a calorimetric jacket and a specially fabricated heat meter (a multijunction differential thermocouple).

The specific features of nitrogen tetroxide required the introduction of certain changes into the design of the existing experimental installation.

Because of the high corrosive activity of N_2O_4, attention was paid to ensuring that the entire sealed circuit of the installation was made of

Table 1

Experimental values of the enthalpy increment of nitrogen tetroxide, obtained directly in the experiments*

P, kg/cm^2	T_{in}, °K	T, °K	Δi, kcal/kg	P, kg/cm^2	T_{in}, °K	T, °K	Δi, kcal/kg
50	282,847	344,93	24,85	125	283,024	424,30	82,27
50	283,066	377,23	41,60	125	282,925	427,08	88,04
50	283,041	378,18	41,82	125	283,087	427,37	88,19
50	298,234	382,23	39,22	150	283,144	430,59	102,82
50	297,999	377,07	35,73	150	283,394	433,81	148,83
50	282,834	397,43	55,95	150	283,424	434,16	150,49
50	282,861	397,85	56,34	150	283,487	438,35	162,91
50	283,846	414,99	170,68	200	282,846	398,26	54,08
50	297,973	416,91	167,27	200	282,978	413,34	66,69
50	298,802	458,20	229,55	200	283,067	426,40	82,04
75	282,864	398,46	56,03	200	282,811	343,74	23,92
75	282,993	413,26	70,01	300	282,804	343,84	24,14
100	282,808	344,28	24,25	300	283,050	379,45	41,08
100	283,044	378,36	41,13	300	283,282	396,25	52,06
100	283,038	378,92	41,50	300	282,890	428,69	81,93
100	283,293	395,83	53,04	300	282,820	345,09	23,70
100	282,860	413,95	68,47	300	283,066	379,39	40,49
100	283,039	429,46	95,80	300	283,242	398,70	52,79
100	283,039	429,46	96,29	300	282,898	423,71	72,79
102,3	282,852	398,47	54,74	300	232,833	345,71	23,83
102,3	282,958	413,53	67,90	300	232,860	345,61	24,06
102,3	282,965	413,57	68,31	300	283,068	379,04	39,47
102,3	282,984	424,06	81,80	300	283,358	404,19	54,83
				300	282,846	419,48	66,17

steel 1Kh18N9T, using argon-arc welding or special detachable joints. Measurement of the mass flow rate of the substance in the circuit was carried out by the calorimetric method, for which, as is known, it is necessary to have data on the heat capacity C_p at the parameters in the flowmeter. For nitrogen tetroxide in the liquid phase at a pressure of 1 kg/cm^2, we experimentally obtained data on the heat capacity C_p, using a calorimetric flowmeter on a separate stand with gravimetric measurement of the mass flow rate of the substance. The available P—V—T data for the liquid at high pressures (^{4}) near the normal boiling temperature made it possible, through known thermodynamic relations, to calculate the heat capacity C_p in the liquid phase for the pressures of the experiment:

$$C_p(T_{\text{av}}, p) = C_p(T_{\text{av}}, 1) - T_{\text{av}} \int_1^p \left(\frac{\partial^2 v}{\partial T^2} \right)_p dp, \tag{2}$$

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* In processing the data, the calculation is carried out in thermochemical calories.

where T_{av} is the average temperature in the calorimetric flowmeter.

Since N_2O_4 has a normal boiling point of 21°, reliable calorimetry in the flowmeter required a temperature level of 0–10°, which necessitated the use of a special refrigeration machine and a special approach to the conditions of calorimetry and thermostating.

Much attention was paid to the purification of nitrogen tetroxide before carrying out the experiment and to the systematic analysis of the purity of the substance under study.

As a result of the experiment, 48 enthalpy values were obtained on isobars of 50, 75, 100, 102.3, 125, 150, 200, and 300 kgf/cm^2 at temperatures from 340 to 460 K (Table 1).

It should be emphasized that, in addition to a detailed study of the liquid phase of nitrogen tetroxide, the near-critical region was investigated in the indicated pressure interval, and data were obtained at supercritical temperature and pressure.

Analysis of the error of the experimental data obtained showed that the limiting error does not exceed 0.7 kcal/kg and increases in the near-critical region owing to the error in assignment of temperature and pressure. The scatter of the data obtained relative to the smoothing curves is substantially smaller.

The experimental data obtained on the enthalpy of nitrogen tetroxide make it possible to check methods for calculating thermodynamic systems that differ substantially from the ideal-gas state, and may be used in engineering for thermal calculations of the corresponding apparatus.

Institute of High Temperatures
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.