

THERMOPHYSICAL PROPERTIES OF A DISSOCIATING COOLANT WITH
A NITROGEN TETROXIDE BASE FOR ATOMIC POWER STATIONS

V. B. Nesterenko, V. P. Bubnov,
and G. G. Kuleshov

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The Soviet Union is conducting a successful program for the accelerated development of atomic power in the European part of the country. The first stage of this program is based on atomic power stations with thermal-neutron reactors of the channel and shell types. Taking account of the limited natural reserves of uranium and the low efficiency of its utilization in thermal-neutron reactors, the future development rates, scales, and economic characteristics of nuclear power will be determined largely by the success achieved in building fast reactors which permit realization of the process of expanded regeneration of nuclear fuel from the tailings of natural uranium and an increase in the efficiency of utilization of the nuclear fuel by a factor of 30 or 40.

The special properties of the physical processes in fast reactors and the requirement of accelerated production of secondary nuclear fuel has made necessary an increase in the nuclear concentration of fissionable fuel and a considerable increase in the specific heat generation in the active zone (by a factor of 5-10, i.e., up to 500-1000 kW/liter) in comparison with thermal-neutron reactors [1]. The characteristics of the breeding process and the doubling time are determined to a large extent by the nuclear and thermophysical characteristics with regard to heat removal of the coolant selected. Investigators are familiar with the results of tests and physical characteristics of experimental atomic power stations using fast reactors with sodium, and with the difficulties encountered in the heat-conversion scheme as a result of the incompatibility of sodium with water in steam generators [1,2]. One of the promising ways of constructing gas-cooled fast reactors with low doubling time is the use of dissociating nitrogen tetroxide as the coolant and the working fluid in single-loop atomic power station schemes. The presence in the dissociating coolant of the reversible chemical reactions



leads to the appearance of an additional concentration mechanism of heat transfer and increases by a factor of 2-3 the heat removal in the active zone of the reactor. The temperature range of the dissociation and recombination reactions and the comparatively low heat of liquid-gas phase transition make it possible to realize with N_2O_4 a gas-liquid cycle with higher heat regeneration than with H_2O or CO_2 , and consequently to obtain better thermodynamic indicators. Atomic power stations with gas-cooled fast reactors and dissociating coolant can be widely used for generating low-cost electric power, producing secondary nuclear fuel, and supplying heat to industry and general consumers.

At the Nuclear Power Institute of the Academy of Sciences of the Belorussian SSR, in cooperation with a number of scientific institutions — the OFTPE of the Ural Science Center of the Academy of Sciences of the USSR, the Thermophysics Institute of the Siberian Branch of the Academy of Sciences of the USSR, the High-Temperature Institute of the Academy of Sciences, the S. M. Kirov Kazakh State University, the Physics Institute of the Daghestan Branch of the Academy of Sciences of the USSR, and others — there have been comprehensive and continuing studies of the thermophysical properties of dissociating nitrogen tetroxide in the range of parameters of its practical use as a coolant and a working fluid for atomic power stations: at temperatures of 293-820°K and pressures of 1-20 MPa. The result of this investigation, coordinated by the Working Group on the Thermophysical Properties of Nitrogen Oxides of the Soviet Commission on Thermodynamic Tables of Technologically Important Gases of the Academy of Sciences of the USSR and by the State Service of Standard Handbook Data of the USSR, has

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been the publication of surveys and handbooks on the physicochemical and thermophysical properties of dissociating nitrogen tetroxide [3-5]. The intensity of experimental and theoretical investigation in this area — of the more than 500 publications on this subject known to the authors, two-thirds have appeared during the past 10 years — makes it desirable to conduct a systematic analysis of all the results obtained, in order to complete within a short time the compilation, with accuracy acceptable for practice, of complete tables of the thermophysical properties of one of the most promising coolants for atomic power stations. We shall discuss the main results of the investigations already conducted and the problems to be solved by further investigations.

Thermochemical Constants and Ideal-Gas Functions. The principal thermochemical constants (heats and entropies of formation, etc.) of all components of the chemically reacting system (1) have been established fairly reliably and are given in [3] (see also the survey [4]). Ideal-gas functions of a mixture have been considered in detail in a study by Bazhin [6]. In order to calculate the composition of a chemically reacting mixture, polynomials describing the variation of the equilibrium constants of the first and second stages of the reaction as functions of temperature have been obtained [5]. A special feature of the chemically reacting system under consideration is the practically complete equilibrium of the first stage of the reaction and the serious imbalance in the second. This last fact has necessitated the development of special methods for calculating the thermophysical properties, taking account of the kinetics of the chemical reactions [7].

Thermodynamic Surface of States. Up to the present time the thermodynamic surface of states of the chemically reacting system (1) has been studied experimentally in considerable detail: investigators have determined the principal properties in the solid, liquid, and gaseous phases and established the parameters of solid-gas and liquid-gas equilibria [5]. Parallel with the accumulation of experimental material on the volumetric behavior of the system in the liquid and gaseous phases, attempts have been made to construct the equations of state for particular regions of the parameters: A. G. Tabachnikov and S. M. Mezheritskii (1969); V. P. Bubnov and V. V. Moiseenko (1970); G. G. Kuleshov and É. É. Shpil'rain (1972); P. M. Klepatskii and V. F. Shankin (1975). In the last interpolation equation of state [8], high accuracy was achieved in describing the available experimental P-V-T data over the entire experimentally investigated range of parameters in the gaseous phase ($T_s \leq T \leq 570^\circ$) with a maximum error of $\sim 0.5\%$. At the same time, the problem of constructing the equation of state in the gaseous phase cannot be regarded as completely solved, since the pressure is not an analytic function of the density for systems which react according to the scheme of dissociation with regrouping (the second stage of the reaction); this was shown by Semenov [9]. Attempts to use the traditional virial expansion on such systems will inevitably lead to an "infinite" second virial coefficient. In [10] it was shown that this effect can be experimentally observed in dissociating nitrogen dioxide at $T \sim 1000^\circ\text{K}$ and $P \sim 0.5\text{--}5\text{ MPa}$. The question of the equation of state in the liquid phase, despite the well-known work of A. G. Tabachnikov [11], can be solved only by the simultaneous processing of P-V-T and C_V experimental data, since the curvature of the experimental isochores in liquid nitrogen tetroxide is commensurable with the error of the P-V-T measurements. Important results concerning the nature of the chemically reacting system (1) in the region of metastable states were obtained in [12,13], the authors of which determined the maximum allowable overheat values for a liquid without formation of a vapor phase, as well as the continuity and monotonicity of the thermodynamic derivatives where the phase equilibrium curves intersect, and also studied the kinetics of the spontaneous and γ -ray-induced boiling of overheated dissociating nitrogen tetroxide.

Caloric Properties. Experimental and theoretical investigation of heat capacity at constant pressure cover practically the entire range of parameters for which it is assumed possible to use a dissociating coolant in the elements of power stations. A detailed survey of the work done in this field is given in [5]. Among the latest studies we may note [14], which, on the basis of the theory of scale transformations, determines the critical index for the isobaric heat capacity and obtains an equation for the slopes of the supercritical maxima of C_p on the basis of experimental data of [15,16]. The only region not covered by any experiment is the region of the liquid state at high pressure, for which the values of the heat capacity were determined from enthalpy measurements. There are as yet no experimental data available on the heat capacity at constant volume, a fact which, as mentioned earlier, prevents a complete solution of the problem of the equation of state in the liquid phase, as well as a reconciliation of the data on volumetric behavior, heat capacity, and

the velocity of sound in the zone of the liquid-gas phase transition. Independent measurements of C_V are now being made at the Nuclear Energy Institute of the Academy of Sciences of the Belorussian SSR and at the Physics Institute of the Daghestan Branch of the Academy of Sciences of the USSR. The enthalpy of dissociating nitrogen tetroxide has been experimentally investigated mainly in the liquid phase [17], but a limited number of experimental points in the gaseous phase have been used for verifying the reliability of the enthalpy calculations: in the temperature range $T_s \leq T \leq 300^\circ\text{K}$ and pressures of up to 10 MPa, this was done by the equation of state of [8], for $P \geq 10$ MPa and up to 770°K by integrating the heat capacity C_p , and for temperatures above 770°K by the method of [18]. Calculations for the entropy of N_2O_4 were carried out in a similar manner [5].

Transfer Properties. The viscosity of the chemically reacting system (1) has been investigated in detail in the liquid phase by the rolling-ball method, and in the gaseous phase by the falling-load and oscillating-disk methods and in a spiral capillary [5]. The smoothed tabulated data on viscosity in the liquid phase have a dispersion of $\sim 8\%$, but according to our estimates, we may expect these values to be systematically low by 10-20%; in the gaseous phase, for $P = 0.1$ -14 MPa and $T = 300$ - 700°K the relative error does not exceed 3%, and the relative error of the calculated data for $T \leq 1000^\circ\text{K}$ and $P = 16$ -25 MPa may reach 7%. The reliability and completeness of the data on viscosity may be considered satisfactory in the first approximation. The parameters of intermolecular interaction of the components of the mixture (1) have been determined on the basis of experimental data by the four-parameter least-squares method in combination with the method of successive approximations [5,19]. Experimental investigation of the thermal conductivity of system (1) are fairly extensive, and a complete survey and analysis of these is given in [5]. An important feature of the calculation of the thermal conductivity of chemically reactive systems is the need to take into account the heat transferred in the form of chemical enthalpy by concentration diffusion. And depending on the ratio of the chemical relaxation times and the characteristic diffusion time, the values of thermal conductivity may vary from frozen to equilibrium values. The thermal conductivity in the gaseous phase has been calculated with due regard to the effect of the nonideal nature of the system on the quantities determining the thermal conductivity of the dissociating gas (density, composition, enthalpy, binary coefficients of diffusion, frozen component of thermal conductivity) [20]. The relatively high errors in the determination of thermal conductivity in the liquid ($\sim 4\%$) and gaseous ($\sim 8\%$) phases [4] makes it impossible to regard these data as exhaustive, especially because of the use of a modified coolant (N_2O_4 with admixtures of NO), whose thermal conductivity, as is shown by the first experimental data, does not differ from the thermal conductivity of pure nitrogen tetroxide determined with an equal error.

Coolant with Technological Impurities. The practical utilization of dissociating nitrogen tetroxide in the pure state is difficult because it is chemically active and hygroscopic. This latter feature leads to the formation of nitric acid, whose presence, owing to the large difference between the boiling points of HNO_3 and N_2O_4 , may seriously increase in percentage terms in zones of phase transition [21], and to a sharp increase in the rate of corrosion of the structural materials used. The reaction forming nitric acid through the absorption of atmospheric moisture by the nitrogen tetroxide can be displaced in the direction of the original substances by introducing into the coolant a relatively small superstoichiometric amount of NO , the reaction product. The use of this modified coolant has proved its advantages over pure N_2O_4 from the viewpoint of corrosion properties [5], but this required a special study of the entire complex of its thermophysical properties. For N_2O_4 - NO solutions over a wide range of concentrations of nitric oxide (NO) the ideal-gas functions were calculated, the parameters of the solid-gas and liquid-gas phase equilibria were established, and the heat capacity C_p , the kinetics of the liquid-gas phase transition, and the thermal conductivity were investigated experimentally [5]. Some estimates (the parameters of the liquid-gas phase equilibrium, density, viscosity) and experimental results (surface tension) were also obtained for N_2O_4 - HNO_3 solutions over a broad range of concentrations [5,22,23]. A problem that remains timely is that of the experimental investigation of most of the thermophysical properties of an N_2O_4 -based coolant over a wide range of concentrations and over the entire region of parameters of its practical utilization. A problem of the first importance is the study of the physicochemical and thermophysical properties of dissociating nitrogen tetroxide with industrial additives of HNO_3 , NO , and others in the zone of phase transitions and the near-critical region. High accuracy in the measurement of the thermophysical properties in the true sense and the composition of the investigated solutions must be regarded

as being among the most important aspects of the investigation. A complex program of such research is now being carried on at the Nuclear Power Institute of the Academy of Sciences of the Belorussian SSR.

Corrosion of Structural Materials in a Coolant Medium. Problems relating to the corrosion resistance of structural materials, and especially the jackets of the heat-generating elements, are very important in the choice of coolant: even for relatively low rates of corrosion, which are not at all dangerous from the viewpoint of the strength properties of the material, a limiting factor may be constituted by the accumulation of the solid phase in the coolant, which in turn may cause erosion of the elements of the installation or clogging of narrow segments of the coolant loop [5]. The corrosion resistance of a broad spectrum of materials in an N_2O_4 -based coolant for temperatures ranging from room temperature to $950^\circ K$ and pressures of up to 16 MPa has been investigated in fairly great detail up to the present time; under these conditions most stainless steels have a high corrosion resistance and similar patterns of behavior of the corrosion rate as a function of time, temperature, pressure, and flow rate [5]. Typical data on the comparative rates of corrosion of stainless steels in an N_2O_4 medium [3] and in air [24] at a temperature of $850^\circ K$ for 1000 h give convincing evidence in favor of the former. At the same time, there is a relatively narrow region of temperatures of the phase transition of technological nitrogen tetroxide containing water or nitric acid as an impurity in which the rate of corrosion of the steels increases by one order of magnitude when the HNO_3 concentration in the liquid-gas phase transition zone increases by a few percent. The corrosion rate in zones of boiling and condensation of the coolant can be substantially reduced, as mentioned earlier, by adding a superstoichiometric amount of NO [5]. The problem of the chemical composition of the products of corrosion of chrome-nickel steels in an N_2O_4 medium remains very important. The few available investigations in this area [5] indicate that the structure of the oxides and oxy salts of the metals making up the steels of structural materials becomes more complex as the temperature decreases, from Fe_2O_3 at $T \sim 600^\circ K$ to $Fe_2O(NO_3)_4 + [NO_2^+][Fe(NO_3)_4^-]$ at $T \sim 300^\circ K$ for iron, the main component. Compounds of the form $Ni(NO_3)_4$, $Zr(NO_3)_4$, and some others have also been found. In future investigations of the complex low-temperature structures of the products (ferrites, nitrate complexes, and mixtures of these) it should be borne in mind that their formation depends to a large extent on the thermal regime and the characteristics of the surface layer of the steels.

Thus, it can be asserted that a number of theoretical problems involved in the preparation of project studies for power installations using dissociating nitrogen tetroxide have been solved thus far on the basis of the accumulated information concerning its thermophysical properties. The solution of most of the problems discussed in this survey should facilitate a more careful analysis of some specific technological aspects of the problem of utilizing dissociating gases as coolants in large-scale power generation.

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