EXPERIMENTAL STUDY OF THE THERMAL CONDUCTIVITY OF NO_2Cl

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The author presents experimental data on the thermal conductivity of NO_2Cl obtained by the hot wire method in the temperature range 280–450° K at pressures up to 10^5 N/m^2.

The thermal conductivity λ of NO_2Cl has still not been thoroughly investigated. The substance is of interest because it undergoes thermal dissociation at relatively low temperatures. Upon heating to 370° K marked decomposition is observed in accordance with the formula

$$2NO_2Cl \rightleftarrows 2NO_2 + Cl_2. \quad (a)$$

At 450° K decomposition into NO_2 and Cl_2 is practically complete. Since at normal pressure nitrogen peroxide molecules exist up to a temperature of the order of 420° K in the form of the dimer N_2O_4, up to 450° K reaction (a) proceeds in accordance with the formula

$$2NO_2Cl \rightleftarrows \underset{\underset{N_2O_4}{\uparrow\downarrow}}{2NO_2} + Cl_2. \quad (b)$$

Thus, at temperatures up to 450° K, convenient for measurements, the system is characterized by the presence of two simultaneous reactions. This makes it possible to check the theoretical ideas of Batler and Brokaw [1] concerning the thermal conductivity of a gas mixture in which more than one equilibrium chemical reaction exists at the same time.

In our experiments we employed the hot wire method to determine the thermal conductivity of NO_2Cl. The apparatus (see [2]) was made of molybdenum glass except for the quartz jacket and the measuring tube. Since the apparatus was intended for studies in the high-temperature region, the measuring tube was also made of quartz.

The resistance thermometers (outer, wound onto the outside surface of the quartz tube, and inner, which served at the same time as a heat source) were made of EPL-1 platinum wire. The ratio $R_{100}/R_0 = 1.3922$. The wire was centered with short quartz sleeves and a nichrome spring. The tension on the spring was about 5 g.

The measuring tube had the following dimensions: inside diameter 3.24 mm; outside diameter 4.75 mm; wire diameter of inner and outer resistance thermometers 0.105 mm; length of measuring section 103.8 mm.

The tube with the resistance thermometers was placed in a quartz jacket connected by means of an adapter (from quartz to molybdenum glass) with a glass head fitted with sealed-in platinum lead-outs, to which the platinum leads from the resistance thermometers were connected.

The quartz jacket with the resistance thermometers was placed in a thermostat, so that the working section of the measuring tube was located in the most uniform region of the temperature field. The thermal conductivity was investigated up to 373° K in the liquid, and at higher temperatures in the air thermostat.

Since the test substance has a boiling point of 258° K, this determined the method of filling the working space of the apparatus. Weighed amounts of NO_2Cl gas in the condensed state were placed in glass ampuls. The ampul with the test substance was sealed, weighed, and placed in a mechanical opener, rotation of which opened the ampul.

The pressure in the system was measured with a manometric molybdenum spiral connected as a null detector. The use of this manometer made it possible to avoid complications due to possible chemical interaction between the test gas and mercury.

The NO_2Cl used in the experiments was obtained by a laboratory method [3] with successive double or triple distillation. The purity of the test gas was checked by measuring the vapor pressure of the liquid phase and, moreover, before the experiments the ampul containing the test substance was cooled with liquid nitrogen. The presence of white crystals of NO_2Cl in the ampul indicates that the test gas has a high degree of purity.

The following corrections were incorporated in the experimentally determined values of λ: for radiation, heat loss from the ends, eccentricity effect, and temperature drop in the wall of the measuring tube.

Corrections were not made for the temperature jump and convection. There was no convenction since in all the experiments the product GrPr was less than 1000.

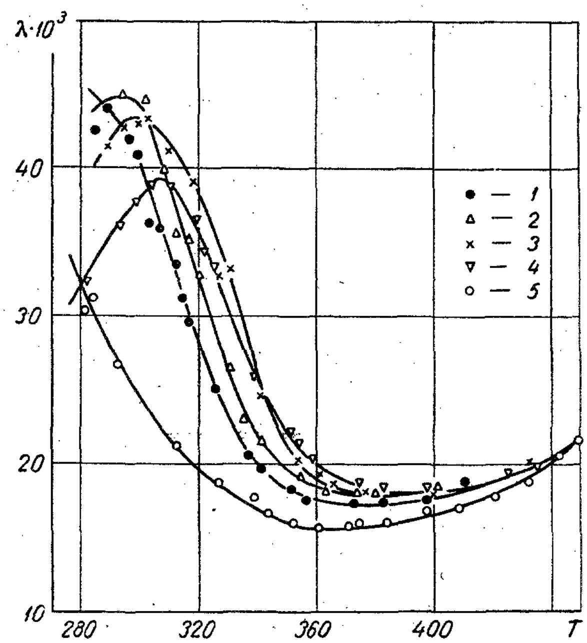
The results of measurements of the thermal conductivity of NO_2Cl are presented in the figure.

Unfortunately, it was not possible to compare the experimentally obtained heat conductivities with the theoretical values since at present there are no initial data for calculations based either on the equilibrium constant or on other parameters characterizing the composition of the gas mixture. The only point that can be calculated is that at a temperature of 450° K, where complete decomposition takes place. The calculation was based on Brokaw's formula [4]

$$\lambda_{cm} = 0.5(\lambda_{cm_1} + \lambda_{cm_2}), \quad (1)$$

which apparently gives the same result for λ_m as the more complicated relations of Lindsay and Bromley [5]. Here, λ_{m1} and λ_{m2} are the mean thermal conductivities determined from the laws of mixture:

$$\lambda_{cm_1} = x_{NO_2}\lambda_{NO_2} + x_{Cl_2}\lambda_{Cl_2} \quad (2)$$



Temperature dependence of thermal conductivity λ, W/m · deg) of NO_2Cl at different pressures: 1) at p = 1.3 · 10^4 N/m^2; 2) 2.7 · 10^4; 3) 5.3 · 10^4; 4) 8 · 10^4; 5) 10^5.

and

$$\lambda_{cm_2} = x_{NO_2}/\lambda_{NO_2} + x_{Cl_2}/\lambda_{Cl_2}. \quad (3)$$

The component λ_{NO_2} was computed with allowance for the usual Eucken correction, λ_{Cl_2} was taken from [6]. The mole fractions x_{NO_2}, x_{Cl_2} were taken from the conditions of complete decomposition of the NO_2Cl molecules on the assumption that at this temperature there is no dissociation of the NO_2 molecules. The results for the calculated values λ_m and experimentally obtained values λ_e for a mixture consisting of the decomposition products of NO_2Cl at a temperature of 450° K and a pressure of 10^5 N/m^2 are $x_{NO_2} = 0.666$; $x_{Cl_2} = 0.333$; $\lambda_{NO_2} = 26.9 \cdot 10^{-3}$; $\lambda_{Cl_2} = 13.7 \cdot 10^{-3}$; $\lambda_m = 21.4 \cdot 10^{-3}$; $\lambda_{exp} = 21.6 \cdot 10^{-3}$.

Hence it is clear that the experimental and calculated data are in quite good agreement. The discrepancy does not exceed 1%.

However, if we compare the results obtained for the thermal conductivity of NO_2Cl with the experimental data for dissociating N_2O_4 molecules [2], we find that they lie considerably below the latter. It is also noteworthy that here the law of variation of thermal conductivity at constant pressure observed in gas mixtures with one chemical reaction (where the curves of variation of thermal conductivity with temperature at p = const for high pressures are displaced in the direction of high temperatures) no longer holds. It is clear from the figure that the curve of variation of thermal conductivity at a pressure of 10^5 N/m^2 has the greatest displacement in the direction of low temperatures.

This indicates that the mechanism of heat transfer in systems with several simultaneous reactions is much more complicated than in systems with one reaction only. In all probability, the fact that the experimental data on λ for NO_2Cl are lower than the thermal conductivity of N_2O_4 can be attributed to the relative slowness of the dissociation reaction of the NO_2Cl molecules. The activation energy of this substance is of the order of 27 000 cal/mole [7]. Essentially, the effect of increased thermal conductivity is due mostly to dissociation of N_2O_4 molecules in the presence of NO_2Cl and Cl_2 molecules. These conclusions are in agreement with the results of [8], in which a study was made of the effect, an inert argon or helium admixture on the thermal conductivity in the dissociating system $N_2O_4 \rightleftarrows 2NO_2$.

NOTATION

λ is the thermal conductivity; λ_e, λ_m are the experimental and calculated values of thermal conductivity; λ_{m1}, λ_{m2} are the mean thermal conductivities determined from the laws of mixture; λ_{NO_2}, λ_{Cl_2}, x_{NO_2}, x_{Cl_2} are the thermal conductivities and mole fractions for NO and Cl_2, respectively; R_0, R_{100} are the resistances of platinum thermometers at temperatures of 0 and 100° C, respectively; Gr is the Grashof number; Pr is the Prandtl number; T, °K are the reference temperatures.

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