# THERMAL CONDUCTIVITY OF THE SYSTEM $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$

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Experimental data on the thermal conductivity of dissociating nitrogen tetroxide have been obtained by the hot-wire method in the temperature range from 290 to 870° K at pressures up to $10^5$ N/m$^2$.

There have been a number of studies of the thermal conductivity of nitrogen tetroxide [1–3]. The data of Srivastava and Barua [2] at pressures up to $6.7 \cdot 10^4$ N/m$^2$ and temperatures in the range from 305 to 363° K cover the reaction $N_2O_4 \rightleftarrows 2NO_2$. In [1, 3] the temperature range was extended to 473° K.

We have investigated the thermal conductivity of the same substance at pressures up to $10^5$ N/m$^2$ over a broad temperature range (290–870° K). This has enabled us to obtain, on the same apparatus, experimental data on the thermal conductivity of a reacting gas mixture with the two successive reversible chemical reactions

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

These reactions are characterized by different rates of the chemical processes [4, 5].

In our investigation we used a basic variant of the "hot-wire" method. As the hot-wire material we used platinum. In the case of nitrogen dioxide the gas was in contact with the platinum wire. Since nitrogen dioxide is a poor conductor of electricity [6], no serious error is introduced into the electrical measurements by placing the leads directly in the gaseous medium.

We still lack complete information regarding the role of platinum in the chemically reacting system $2NO_2 \rightleftarrows 2NO + O_2$.

Investigations made at the State Scientific Research and Planning Institute of the Nitrogen Industry indicate that the effect of the platinum is only slight and incapable of seriously distorting the accuracy of the results.

The apparatus was described in [7], where the first results on the thermal conductivity of the system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ were obtained and discussed. These data have now been refined and supplemented. Since the apparatus has already been described [7], we will merely mention its principal components.

The working section is a calibrated tube of quartz glass, inside diameter 3.24 mm, outside diameter 4.75 mm. The tube and resistance thermometers are placed in a quartz vessel joined by an adapter (from quartz to molybdenum glass) with a glass head to which the platinum leads from the resistance thermometers are connected. The diameter of the resistance thermometer wire is 0.105 mm; the length of the measuring section is 103.8 mm.

In making the resistance thermometers we used chemically pure platinum wire grade PL-1. The ratio $R_{100}/R_0 = 1.392$. All the conductors were soldered with gold. The tension was maintained in the wire during operation by means of a nichrome spring outside the high-temperature zone. The tension on the spring was about 5 g.

The voltage drop in the circuit was measured with a class 0.015 R-300 high-resistance potentiometer.

Below 373° K, the temperature of the working section was controlled by means of a liquid bath. This enabled us to measure the $\lambda$ of the system $N_2O_4 \rightleftarrows 2NO_2$ with the necessary temperature step and make a very accurate determination of the non-monotonic variation of the thermal conductivity with temperature.

At temperatures above 373° K, the measurements were made in a thermostatic system consisting of a copper block, thermal insulation, a three-segment heater, and a temperature monitoring and regulating unit. The uniformity of the temperature field was monitored by means of three chromel-alumel thermocouples arranged inside the block on a length of 300 mm. The temperature nonuniformity on this length did not exceed 0.3° K. The pressure in the system was measured correct to 1 mm Hg with a manometric molybdenum spiral [7, 13] employed as a null detector. The use of this manometer enabled us to avoid interaction between the gas and mercury; when nitrogen dioxide comes into contact with a mercury surface, nitrates of monovalent and divalent mercury are formed with the liberation of nitric oxide [8].

The nitrogen dioxide employed was obtained under factory conditions and then purified. To this end the liquid ditetroxide was dried with phosphorus pentoxide, mixed with nitric acid (d = 1.51 g/cm$^3$) in the ratio of 1 : 1 by volume, and distilled in a stream of oxygen over phosphorus pentoxide. The dry, freshly distilled ditetroxide had a melting point of 261.9° K and a boiling point of 294.3° K. The purity of the investigated gas was estimated at 99.8%.

As a check, after each individual series of measurements with nitrogen dioxide we made control measurements of the $\lambda$ of air at atmospheric pressure. In all cases the deviation from reliable published data [9] was not more than 1%, which indicated that the apparatus was functioning normally.

These experiments enabled us to extend the range of investigation of the system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$ to pressures of $10^5$ N/m$^2$ and temperatures up to 870° K. Under these conditions, the $N_2O_4$ molecules break down completely to $NO_2$, and at a temperature on the order of 870° K the dissociation of $NO_2$ ceases.

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

No correction was made for convection, since in all the experiments the product GrPr was much less than 1000.

The accuracy of the experimental data was estimated at about 2.9%. The systematic and random measuring errors amount to 1.5%. In analyzing the data we did not take into account the effects of thermal diffusion and the temperature jump. According to our estimates these errors apparently do not exceed 1.4% for the range of temperatures and pressures investigated.

The results of the measurements are presented in the table, while the data and calculations for a pressure of $10^5$ N/m$^2$ are also shown in the figure.

The thermal conductivities were calculated both with allowance for the contribution of the chemical reaction on the assumption of local and chemical equilibrium (solid line in the figure) and for a mixture that was chemically "frozen" but of equilibrium composition (dashed line). Formulas for the λ of chemically reacting gases are presented in [2, 3, 7].

It is clear from the figure that for the first stage of the chemical reaction ($N_2O_4 \rightleftarrows 2NO_2$) the experimental and calculated data are in satisfactory agreement.

For the second stage ($2NO_2 \rightleftarrows 2NO + O_2$), which proceeds at temperatures above 420° K, there is a substantial departure from the calculations made on the assumption of local chemical equilibrium. Much better agreement is obtained for a "frozen" gas mixture of equilibrium composition.

It should also be noted that in the region of dissociation of the $NO_2$ molecules the measured λ do not depend on pressure.

The departure of the second-stage process from the curve calculated with allowance for the effect of the chemical reaction is attributable to the fact that, under our conditions, the rates of the reaction $2NO_2 \rightleftarrows 2NO + O_2$ are not so great in comparison with the rates of the diffusion processes; thus, the concentration profiles correspond to local chemical equilibrium.

According to Carrington and Davidson [4], who experimentally investigated the kinetics of the process of thermal dissociation $N_2O_4 \rightleftarrows 2NO_2$, the time necessary for chemical equilibrium to be established in this system is much less than for the reaction $2NO_2 \rightleftarrows 2NO + O_2$.

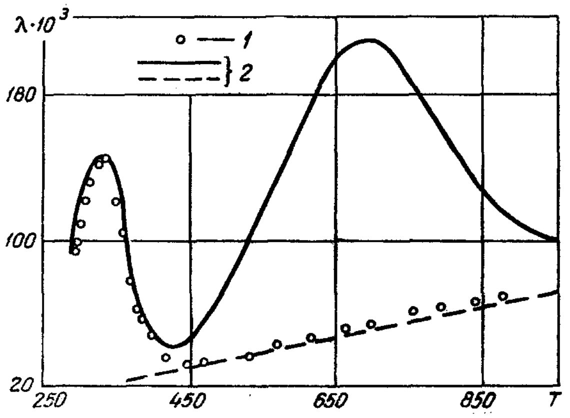
If, however, the results are considered in the light of the work of Secrest and Hirschfelder [10], the reaction $2NO_2 \rightarrow N_2O_4$ with activation energy E = 0 [4] belongs in the class of reactions with rapid establishment of chemical equilibrium. In this case, the chemical processes have an important influence on the thermal conductivity of the reacting gas mixture. The reaction $2NO_2 \rightarrow 2NO + O_2$ with activation energy E = = 105 kJ/mole [11] belongs to the class of slow reactions. This provides a basis, in accordance with [10], for treating the given gas mixture as "frozen" and calculating λ as for a simple mechanical gas mixture.

Experimental Values of the Thermal Conductivity of Nitrogen Dioxide

| $P = 2.7 \cdot 10^4$ N/m$^2$ | | $P = 5.3 \cdot 10^4$ N/m$^2$ | | $P = 8 \cdot 10^4$ N/m$^2$ | | $P = 10^5$ N/m$^2$ | |
|---|---|---|---|---|---|---|---|
| $T$ | $\lambda \cdot 10^4$ | $T$ | $\lambda \cdot 10^4$ | $T$ | $\lambda \cdot 10^4$ | $T$ | $\lambda \cdot 10^4$ |
| 297 | 1388 | 292 | 1236 | 298 | 1040 | 296 | 921 |
| 305 | 1488 | 309 | 1513 | 301 | 1187 | 298 | 980 |
| 318 | 1375 | 321 | 1571 | 306 | 1250 | 304 | 1094 |
| 324 | 1316 | 332 | 1405 | 308 | 1380 | 309 | 1206 |
| 340 | 876 | 345 | 1064 | 315 | 1490 | 318 | 1318 |
| 344 | 792 | 353 | 917 | 320 | 1492 | 332 | 1432 |
| 359 | 540 | 366 | 611 | 322 | 1540 | 337 | 1358 |
| 369 | 428 | 373 | 540 | 346 | 1233 | 350 | 1204 |
| 380 | 370 | 377 | 473 | 365 | 808 | 357 | 1055 |
| 397 | 315 | 386 | 422 | 384 | 509 | 368 | 793 |
| 414 | 298 | 407 | 343 | 391 | 453 | 379 | 616 |
| 434 | 299 | 427 | 323 | 404 | 390 | 382 | 588 |
| 462 | 315 | 454 | 324 | 432 | 344 | 397 | 482 |
| 484 | 332 | 473 | 327 | 443 | 326 | 419 | 360 |
| 498 | 342 | 505 | 353 | 470 | 332 | 448 | 337 |
| 504 | 348 | 538 | 379 | 505 | 356 | 473 | 344 |
| 538 | 376 | 578 | 427 | 542 | 384 | 533 | 378 |
| 579 | 446 | 601 | 443 | 577 | 429 | 567 | 426 |
| 601 | 444 | 628 | 465 | 608 | 453 | 618 | 458 |
| 671 | 536 | 671 | 522 | 635 | 496 | 659 | 520 |
| 688 | 533 | 709 | 543 | 664 | 522 | 698 | 537 |
| 709 | 543 | 757 | 598 | 692 | 580 | 753 | 610 |
| 845 | 644 | 793 | 616 | 739 | 601 | 790 | 620 |
| 858 | 650 | 853 | 668 | 793 | 631 | 838 | 667 |
| 878 | 661 | 876 | 673 | 854 | 675 | 871 | 683 |

The values obtained for the thermal conductivity of nitrogen dioxide are in satisfactory agreement with the data of [2, 3]. The maximum discrepancy does not exceed the limits of accuracy of the experiment.

A comparison of our data with those of Coffin and O'Neal [1] (for the results of these measurements see [12]) at $10^5$ N/m$^2$ showed that the greatest discrepancy (up to 14%) is observed in the region of the thermal conductivity peak in the first stage of the reaction ($N_2O_4 \rightleftarrows 2NO_2$), whereas at 470° K, where the reaction $2NO_2 \rightleftarrows 2NO + O_2$ occurs, the discrepancy is less than 1%. Unfortunately, the reason for this could not be established, since we are unaware of the conditions (geometry of measuring tube, purity of product, etc.) under which Coffin and O'Neal's measurements [1] were carried out.



Temperature dependence of the thermal conductivity (W/m · deg) of nitrogen dioxide at a pressure of $10^5$ N/m$^2$: 1) experiment; 2) calculation.

## NOTATION

$\lambda$ is the thermal conductivity, W/m · deg; $R_0$ and $R_{100}$ are the resistances of the platinum thermometers at 0 and 100° C, respectively; Gr is the Grashof number; Pr is the Prandtl number; T is the experimental temperature, °K; E is the activation energy; d is the density.

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