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CALCULATED EVALUATION OF THE THERMAL PHYSICAL PROPERTIES OF NITROGEN AS A WORKING FLUID OF CRYOGENIC PISTON ENGINES. HEAT CONDUCTIVITY CALCULATION

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Vehicles with internal combustion engines (ICEs) used by many enterprises or high fire hazard facilities (airports, docks, elevators, chemical plants, refineries) can be sources of ignition due to the peculiarity of their technological (work) cycle. Recently, vehicle designers have devoted much attention to power units that are alternatives of ICEs (electric engines, hybrid power units, and cryogenic engines), with the power units being capable of ensuring a higher fire safety in transport. Kreogenic engines as power plants in special vehicles used in the above-mentioned high fire hazard facilities are particularly important. In such engines, the working medium (WM) is liquid nitrogen, and the heat source to implement the work cycle is the warmth of the environment. Nitrogen is the most affordable non-flammable gas, which is why in terms of economic considerations, it is most acceptable for use as WM for a cryogenic piston engine without disturbing nitrogen content balance in the atmosphere. The increased interest in creating cryogenic power units for vehicles determined the relevance of a detailed study of thermodynamic and kinetic characteristics (transfer coefficients) of molecular nitrogen over a wide range of pressures and temperatures. The article presents an original method and the results of calculating the thermal conductivity of nitrogen used as a working fluid for transport piston units. A description of the developed mathematical model of kinetic characteristics in dense molecular media (dense gases and liquids) is presented. The mathematical model and computational procedures are based both on the formal scheme of Enskog and statistical-mechanical approach within the framework of the thermodynamic perturbation theory with no empirical parameters involved. The features of the method are sufficient minimum of initial information, high precision, and applicability for any practically important state ranges. Using gaseous and liquid nitrogen as an example, the calculated values of their thermal conductivity are compared with the available in the literature experimental data at pressures up to 5 MPa in the temperature range from 80 to 300 K. The results of calculations according to the proposed method allow us to predict the kinetic characteristics of nitrogen in experimentally unexplored state ranges up to pressures of 1000 MPa and temperatures up to 5000 K. Errors in the calculation of the thermal conductivity of nitrogen are at the level of ordinary experimental errors.

Keywords: *cryogenic piston engine, nitrogen, kinetic characteristics, working fluid, thermal conductivity, mathematical model.*

Introduction

Vehicles with internal combustion engines (ICEs) used by many enterprises or high fire hazard facilities (airports, docks, elevators, chemical plants, refineries) are sources of ignition due to the peculiarity of their technological (work) cycle. Recently, vehicle designers have devoted much attention to cryogenic piston engines, which can be used as power plants in special vehicles for the above-mentioned high fire hazard facilities [1, 2].

In such engines, the working medium (WM) is liquid nitrogen, and the heat source to implement the work cycle is the warmth of the environment. Nitrogen is the most affordable non-flammable gas (~78% in atmospheric air), which can be used as WM for a cryogenic piston engine without disturbing nitrogen content balance in the atmosphere.

The increased interest in the creation of cryogenic power units for vehicles [1, 2] determined the relevance of a detailed study of thermodynamic [3–5] and kinetic characteristics (transfer coefficients) of molecular nitrogen over a wide range of pressures and temperatures.

Analysis of Studies and Publications

Getting reliable experimental data on the kinetic properties of substances in vast ranges of states is difficult, and in many cases simply impossible. This motivates the development of computational methods to mainly include phenomenological and statistical ones. Among the strict statistical methods, a special place is occupied by the theory of Enskog [6], which combines good mathematical substantiation and simplicity of working formulas.

Method of Calculation

In the present paper, in order to describe the thermal conductivity of dense molecular media, a combined method is proposed, which is the development of the modified Enskog theory with the definition of thermodynamic parameters within the framework of modern perturbation theory schemes [7].

The condensed medium is represented as consisting of solid spherical molecules of diameter σ. Insignificant are triple and higher-order collisions. Due to the fact that the molecules have certain volumes, the following two effects become important during gas compression:

1) Impact transfer of pulse energy: when two spherical molecules collide, the pulse energy is instantly transferred from the center of one molecule to the center of another.

2) Change in the number of collisions per second: on the one hand, the frequency of collisions increases, since σ is not negligible in comparison with the average intermolecular distance. On the other hand, it decreases, since the molecules are so close that they shield each other against incident molecules. Thus, the collision frequency is Y times different from the frequency of collisions in the gas of point particles.

In view of these factors, the collision integral for rarefied gases [6] must be transformed. To modify it, it is necessary to introduce two changes. Firstly, because the colliding molecules are not point-like, their centers do not coincide and, accordingly, the distribution function of an incident particle must be calculated at the point $\mathbf{r}-\sigma\mathbf{k}$, where **k** is a unit vector directed from the center of the incident molecule to the center of the target. Secondly, in dense gases and liquids, the volume per molecule (v) has the same order of magnitude as that of the molecule volume $\frac{4}{3}\pi\left(\frac{\sigma}{2}\right)^3$. Therefore, the volume, in which the center of any single molecule is located, decreases, increasing the probability of collision. Thus, the collision frequency increases by Y times, with Y depending on the density of the number of particles for the system of solid spheres (SS). The function Y can be calculated at the point where two spherical molecules contact, i.e. $\mathbf{r}-\frac{1}{2}\sigma\mathbf{k}$.

Based on these considerations, Enskog finds a new type of the collision integral [6]. From the Boltzmann equation with the collision integral in the form of Enskog, we can determine the SS system function of distribution using the method of decomposition by the collision frequency parameter. Then, through the integrals of this function, we can express the densities of the energy fluxes, pulse, mass and, finally, kinetic coefficients [6]. The result is the following expression of the Enskog theory for thermal conductivity:

$$\frac{\lambda}{\lambda_0 b_0 \rho} = \frac{1}{y} + 1.2 + 0.755y \,. \tag{1}$$

Here, $y = \frac{2\pi\sigma^3}{3}\rho Y = b_0\rho Y = b_0\rho\, g(\sigma)$; $\rho=N/V$ – is the density of the number of particles; $g(r)$ – is the SS system radial distribution function associated with the compressibility factor z as follows:

$$z = \frac{p}{\rho kT} = 1 + y \,.$$

The coefficient λ_0 for rarefied gases, which is included in expression (1), is given in [7] and has the form

$$\lambda_0 = \frac{25}{32\sqrt{\pi}} c_v \sqrt{\frac{kT}{m}} \frac{1}{\sigma^2 \Omega^{(2,2)^*}}, \tag{2}$$

where c_v is the molecular heat capacity $\left(c_v = C_v / N_A\right)$; k is the Boltzmann constant.

It is convenient to reduce this expression to the product of two factors, one of which will be dimensionless and common to various gaseous and liquid media, while the other will include the individual characteristics of each substance. As a potential of interaction, we use the Lennard-Jones (L-J) potential, which belongs to the best simple two-parameter potentials. After replacing $T = ET^*$, we obtain (for monatomic gases)

$$\lambda_0 = \left(10^{-7} \frac{R_0^{3/2}}{n_A \sigma_A^2} \sqrt{\frac{E}{M}}\right)\left(\frac{75}{64\sqrt{\pi}} \cdot \frac{\sqrt{T^*}}{\Omega^{(2,2)^*}}\right), \tag{3}$$

where M=28.0134 kg/kmol is the molar mass of nitrogen; R_0 is the universal gas constant, R_0=8.31441 kJ/(kmol·K); N_A is the Avogadro number, $N_A = n_A \cdot 10^{27}$ 1/kmol (n_A=0.6022045); $\sigma = \sigma_A \cdot 10^{-10}$; m, ε, σ are the parameters of the L-J potential, E=ε/k.

In expressions (2) and (3), $\Omega^{(2.2)*}$ is the L-J system collision integral divided by the SS system collision integral. The integral requires the use of approximation [8].

The ratio

$$\frac{\lambda_0}{\eta_0}\frac{M}{C_v} = f ,$$

where $\eta_0 = \frac{5}{16\sqrt{\pi}}\frac{\sqrt{mkT}}{\sigma^2\Omega^{(2\cdot2)*}}$, is known as the Aiken coefficient. In the one-atom case,

$$\tilde{f} = fC_v = \frac{15}{4}R_0 .$$

In polyatomic gases and liquids, a significant role is played by the rotational and oscillatory degrees of freedom, with the degrees making a significant contribution to heat capacity. In order to take into account these influences, various modifications of the coefficient $\tilde{f}$ are proposed. This scheme uses a simple, but quite reliable, Aiken correction

$$\tilde{f} = R_0\left(\frac{C_v(T)}{R_0} + 2.25\right).$$

Thus, expression (3) takes the form

$$\lambda_0 = \tilde{\lambda}\lambda_0^* , \quad \tilde{\lambda} = 10^{-7}\frac{R_0^{3/2}}{n_A\sigma_A^2}\left(\frac{C_v}{R_0} + 2{,}25\right)\sqrt{\frac{E}{M}} , \quad \lambda_0^* = \frac{5}{16\sqrt{\pi}}\cdot\frac{\sqrt{T^*}}{\Omega^{(2,2)*}}\cdot f_c , \tag{4}$$

where $f_c = \left(C_v^0/R_0\right) + 2.25$; C_v^0 is the heat capacity in an ideal gas state $\left(C_v^0 = C_p^0 - R_0\right)$.

With $C_v/R_0 = 3/2$ expression (4), obviously, transforms into (3).

Although the above-mentioned formulas for thermal conductivity were obtained for the SS system, Enskog showed how they can be modified and applied to real dense molecular media. To do this, it is necessary to redefine the values of b_0 and y [6].

The above equations determine the so-called modified Enskog theory. The kinetic coefficients of a real system can be calculated using only the state equation data obtained within the framework of the original scheme of the modified perturbation theory (MPT) [7].

Next, the following combined method is used: the expressions obtained in the modified Enskog theory are used to calculate the transfer coefficients, and the definition of parameters included there is based on the MPT scheme.

In equation (1), when determining thermal conductivity, it is necessary to independently determine parameters b and y. The compressibility factor z, specifying the equation of state,

$$z = \frac{pv}{N_A kT} = \frac{p^*}{T^*\rho^*} = \rho^*\left[\frac{\partial(\beta\beta f}{\partial\rho^*}\right]_{T^*} .$$

In the further calculations, we restrict ourselves to the first-order MPT, since the corrections introduced, with the members of subsequent orders taken into account, are so small that they go beyond the limits for the precision specified by the existing experimental data.

According to MPT, taking into account the members of the first order, we obtain

$$z = 1 + 2\chi\frac{2-\chi}{(1-\chi)^3} + \sum_{i,k=0}^{3}(i+1)a_{ik}\rho^{*(i+1)}\Big/T^{*(k+1)} , \tag{5}$$

where $\chi = \frac{\pi}{6}\rho d^3 = \frac{\pi}{6}\xi^3\rho^* = 0.4177\rho^*$ is the packing parameter, a_{ik} is the coefficients of the polynomial representation of the group integral $I_1(T^*,\rho^*)$ of the first order of MPT [8].

Comparing (5) with the virial expansion for z, we find the second virial coefficient

$$B = \frac{2\pi}{3} N_A \sigma^3 B^*,$$

$$B = N_A \sigma^3 \left[\frac{2\pi}{3}\xi^3 + \sum_{k=0}^{3} a_{0k} \left(T^*\right)^{-(k+1)} \right].$$

The product $b\rho$ is determined from the expression

$$b\rho = \frac{2\pi}{3}\rho^3 \left[B^*\left(T^*\right) + T^*\left(dB^*/dT^*\right) \right] = 4\chi - \rho^* \sum_{k=1}^{3} k a_{0k} \left(T^*\right)^{-(k+1)},$$

and the parameter y

$$y = 2\chi \frac{2-\chi}{(1-\chi)^3} + \sum_{i,k=0}^{3} (i+1) k a_{ik} \rho^{*(i+1)} / T^{*(k+1)}. \qquad (6)$$

In order to determine B^*, we use approximation [7]

$$B^* = \sum_{s=0}^{9} B_s / T^{*s},$$

which gives an alternative form for $b\rho$

$$b\rho = \frac{2\pi}{3}\rho^* \left[B_0 + \sum_{s=2}^{9} B_s (1-s) / T^{*s} \right], \qquad (7)$$

to be used in subsequent calculations.

The transfer coefficient λ of gases and liquids within the framework of the combined method has the form

$$\lambda = \lambda_0 b\rho \left(\frac{1}{y} + 1.2 + 0.755 y \right),$$

where y and $b\rho$ are determined according to (6) and (7); λ_0 is the thermal conductivity of an ideal gas.

The drive parameter $\tilde{\lambda}$ appearing in (4) has the form

$$\tilde{\lambda} = 125.893 \frac{\sqrt{E/M}}{\sigma^2}, 10^{-3} \text{ W/(m·K)}.$$

The efficiency of the proposed calculation procedure was verified in determining the thermal conductivity of gaseous and liquid nitrogen in the range from cryogenic to room temperature (80 ... 300 K) at pressures up to 5 MPa. The L-J potential parameters have the following values for nitrogen $E=\varepsilon/k=97.31$ K, $\sigma=3.5827\cdot10^{-10}$ m.

In Tables 1, 2, the calculated thermal conductivities of nitrogen in relation to temperature at the pressures P=0.1 MPa and P=5 MPa are compared with the experimental data given in [10–12].

Figs. 1, 2 show the temperature dependence of the thermal conductivity of nitrogen along the isobars P=2 MPa and P=4 MPa in comparison with the experimental data [10–12].

The average values $\overline{\delta} = \sum_{n=1}^{N_\delta} |\delta(T_n)| / N_\delta$ of the deviation moduli $\delta = (\eta^{\text{distr}} / \eta^{\text{exp}}) - 1$ in the specified temperature range for the thermal conductivity are $\overline{\delta}$ =9.6% (2 MPa) and $\overline{\delta}$ =8% (4 MPa).

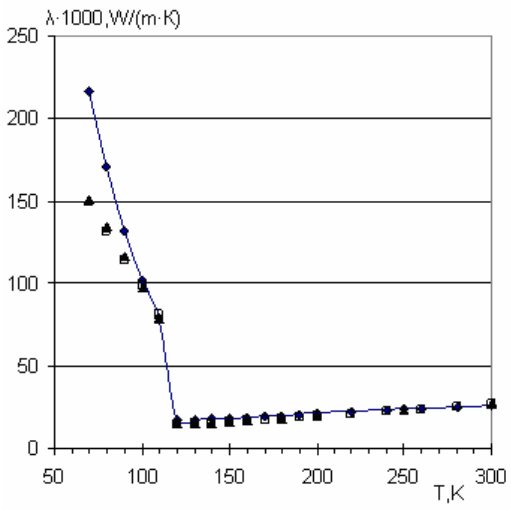
The results of the calculated values of the thermal conductivity of nitrogen are in satisfactory agreement with the experimental data. Thus, the restriction by first-order terms in the obtained MPT expansions provides for errors in the calculations of thermal conductivity, comparable in magnitude with the experimental errors.

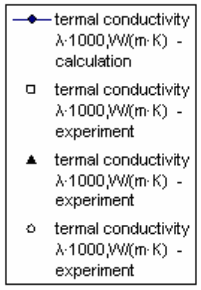
Table 1. Comparison of the experimental and calculated value of the thermal conductivity of nitrogen in relation to temperature at the pressure P=0.1 MPa

T, K	$\lambda\cdot10^3$, W/(m·K) (calculation)	$\lambda\cdot10^3$, W/(m·K) (experiment [10])	δ	$\lambda\cdot10^3$, W/(m·K) (experiment [12])	δ
70	213.96	–	–	–	–
80	8.36	7.82	0.06900	7.82	0.06900
90	9.40	8.63	0.08920	8.63	0.08900
100	10.49	9.58	0.09500	9.58	0.09500
110	11.59	10.48	0.10590	10.40	0.11440
120	12.67	11.30	0.12120	11.30	0.12120
130	13.71	12.00	0.14250	12.00	0.14250
140	14.71	13.00	0.13160	13.00	0.13160
150	15.66	13.90	0.12660	13.90	0.12660
160	16.56	14.80	0.11890	14.80	0.11890
170	17.41	15.70	0.10890	15.70	0.10890
180	18.21	16.60	0.09700	16.60	0.09700
190	18.97	17.50	0.08400	17.50	0.08400
200	19.70	18.30	0.07650	18.30	0.07650
220	21.04	19.80	0.06260	20.00	0.05200
240	22.29	21.30	0.04648	21.40	0.04159
250	22.87	–	–	–	–
260	23.44	22.80	0.02800	22.90	0.02358
280	24.53	24.20	0.01360	24.40	0.00530
300	25.57	25.70	-0.00510	25.90	-0.01300
$\bar{\delta}$	–	–	0.08100 (8.1%)	–	0,08380 (8.38%)

Table 2. Comparison of the experimental and calculated value of the thermal conductivity of nitrogen in relation to temperature at the pressure P=5 MPa

T, K	$\lambda\cdot10^3$, W/(m·K) (calculation)	$\lambda\cdot10^3$, W/(m·K) (experiment [10])	δ	$\lambda\cdot10^3$, W/(m·K) (experiment [11])	δ	$\lambda\cdot10^3$, W /(m·K) (experiment [12])	δ
70	221.54	–	–	152.3	0.6800	–	–
80	175.34	135.0	0.2988	137.4	0.2760	142.0	0.2348
90	136.74	–	–	119.7	0.1420	–	–
100	107.84	–	–	102.3	0.0540	–	–
110	86.03	–	–	85.6	0.0050	–	–
120	68.63	–	–	69.4	-0.0110	–	–
130	53.00	–	–	54.7	-0.0310	–	–
140	26.36	–	–	32.0	-0.1760	–	–
150	24.44	–	–	24.5	-0.0025	–	–
160	23.72	21.8	0.0880	22.7	0.0450	21.8	0.0880
170	23.58	21.6	0.0920	–		21.6	0.0920
180	23.69	21.7	0.0920	22.1	0.0720	21.2	0.1170
190	23.92	22.2	0.0770	–	–	22.6	0.0580
200	24.22	22.4	0.0810	22.7	0.0670	22.4	0.0810
220	24.92	23.2	0.0740	–	–	23.4	0.0650
240	25.69	24.4	0.0528	–	–	24.5	0.0480
250	26.09	–	–	25.2	0.0350	–	
260	26.49	25.6	0.0347	–	–	25.7	0.0310
280	27.29	26.7	0.0220	–	–	26.9	0.0145
300	28.10	27.8	0.0108	28.3	-0.0070	28.0	0.0064
$\bar{\delta}$	–	–	0.0840 (8.4%)	–	0.097 (9.7%)	–	0.0760 (7.6%)





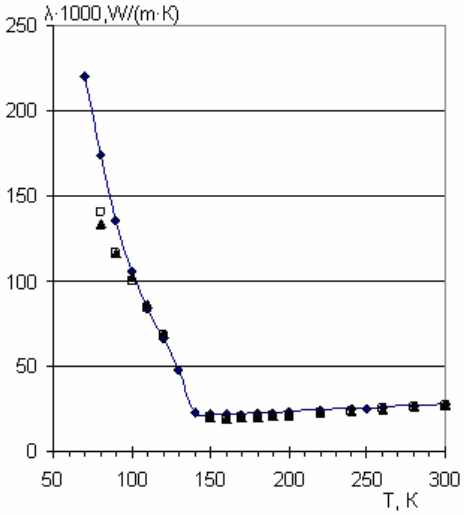


Fig. 1. Thermal conductivity of nitrogen in relation to temperature for the isobar P=2 MPa:
curve – calculation according to the MPT scheme;
symbols – experiment [10–12]

Fig. 2. Thermal conductivity of nitrogen in relation to temperature for the isobar P=4 MPa:
curve – calculation according to the MPT scheme;
symbols – experiment [10, 12]

Conclusions

The proposed method for determining the transfer coefficients of dense gases and liquids is a combined one: the formal Enskog scheme was used for the calculations, and the thermodynamic parameters included in the expressions were determined within the MPT framework. This method was developed to the state that meets engineering requirements and makes it possible to obtain the kinetic characteristics of liquid and gaseous nitrogen, with the characteristics used to develop promising types of environmentally friendly and fireproof vehicles. The features of the method are its applicability for a wide range of states and sufficiency of the initial information minimum. Implemented in the form of a computer software, it provides the operational acquisition of data on the thermal conductivity of nitrogen, including cryogenic one.

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Розрахункова оцінка теплофізичних властивостей азоту як робочого тіла поршневого кріодвигуна. Визначення теплопровідності

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Транспортні засоби з двигунами внутрішнього згоряння (ДВЗ), що використовуються на багатьох підприємствах або об'єктах з підвищеною пожежонебезпекою (аеропорти, доки, елеватори, хімічні заводи, нафтопереробні підприємства), можуть являти собою джерела займання через особливості їхнього технологічного (робочого) циклу. Останнім часом увагу розробників транспортних засобів привертають альтернативні двигунам внутрішнього згоряння силові установки (електродвигуни, гібридні силові установки, а також кріодвигуни), які можуть забезпечити, в тому числі, і більш високу пожежну безпеку транспорту. Кріодвигуни як силові установки набувають особливого значення для спеціальних транспортних засобів, що експлуатуються в структурі вищевказаних пожежонебезпечних об'єктів. Як робоче тіло для кріодвигуна може застосовуватися скраплений азот, а гарячим джерелом для реалізації робочого циклу доцільно використовувати теплоту навколишнього середовища. Азот є найбільш доступним негорючим газом, тому з економічних міркувань він найбільш прийнятний як робоче тіло для поршневого кріодвигуна, за таких обставин не порушується баланс вмісту азоту в атмосфері. Підвищений інтерес до створення кріогенних силових установок для транспортних засобів зумовив актуальність детального дослідження термодинамічних і кінетичних характеристик (коефіцієнтів переносу) молекулярного азоту в широкому діапазоні тисків і температур. У статті наведено оригінальний метод і результати розрахунку теплопровідності азоту, використовуваного як робоче тіло для транспортних поршневих установок. Подано опис розробленої математичної моделі кінетичних характеристик щільних молекулярних середовищ (газів і рідин). Математична модель і обчислювальні процедури грунтуються на формальній схемі Енскога і на статистико-механічному підході в рамках термодинамічної теорії збурень без залучення емпіричних параметрів. Особливостями методу є: достатній мінімум вихідної інформації, висока точність, застосовність для будь-яких практично важливих діапазонів станів. На прикладі газоподібного і рідкого азоту наведено порівняння розрахункових значень теплопровідності з наявними в літературі експериментальними даними для тисків до 5 МПа в інтервалі температур 80–300 К. Результати розрахунків, виконаних за запропонованою методикою, дозволяють прогнозувати кінетичні характеристики азоту в недосліджених експериментально діапазонах станів аж до тиску 1000 МПа і температур до 5000 К. Похибки розрахунків теплопровідності азоту знаходяться на рівні звичайних експериментальних помилок.

Ключові слова: *поршневий кріодвигун, азот, кінетичні характеристики, робоче тіло, теплопровідність, математична модель.*

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