

An empirical equation of state for nitrogen at high pressure and density is considered. It is shown that for nitrogen at densities greater than  $0.6 \text{ g/cm}^3$ , by using available data [1-3] on static compression of gaseous nitrogen and shock compression of liquid nitrogen, it is possible to construct a Mie-Grüneisen type equation of state which gives a pressure-density relationship close to experiment along the shock adiabat of liquid nitrogen and agrees with the calculations of other authors for temperature values beyond the shock-wave front [2-3]. Heat capacity, entropy, and Grüneisen coefficient values beyond the shock-wave front in liquid nitrogen are calculated.

## 1. Introduction

Statistical methods for finding the equation of state of a dense substance have not yet led to formal solutions, although they have proved useful in a number of approximate numerical computations. The virial theorem of classical mechanics is at present effective only at low and moderate densities [4, 5], while cell and hole methods do not always produce satisfactory agreement with experiment [2, 5]. Thus, in practical calculations simpler equations of state are usually employed [6-8]. The most widely used is the Mie-Grüneisen equation, usually written in the form

$$E(P, \rho) - E_x(\rho) = [P - P_x(\rho)]/\rho\Gamma(\rho), \quad (1.1)$$

where the index  $x$  indicates terms connected with cold compression of the substance, and  $\Gamma(\rho)$  is the Grüneisen coefficient, weakly dependent on density. Assuming that the molecules of the dense matter perform small oscillations about equilibrium positions, the dependence of pressure on density and temperature may be derived from Eq. (1.1) as follows [6]:

$$P = \Gamma(\rho) C_V \rho T + P_x(\rho). \quad (1.2)$$

An equation of state of this form provides a good description of shock compression of a number of condensed substances up to high densities [6, 9, 10]. It develops that for nitrogen it is also possible to construct an empirical equation of state of the form of Eq. (1.2), which describes available experimental data well. We note that the equation of state of real van der Waals gases [11] and the equation of state of ideal gases are special cases of Eq. (1.2), although they are derived from different considerations.

## 2. Empirical Equation of State and Shock Adiabat of Dense Nitrogen

Analysis of experimental data [1] on compression of gaseous nitrogen to a density of the order of  $1 \text{ g/cm}^3$  and pressure of 10 kbar indicates that over the entire interval studied the behavior of the nitrogen can be described well by an equation of state similar to Eq. (1.2), while at densities greater than  $0.6 \text{ g/cm}^3$  the following simple relationship is applicable:

$$P \approx (4.3\rho - 10)T + P_x(\rho), \quad (2.1)$$

where  $P_x(\rho)$ , a function dependent solely on density, may be identified with the cold pressure of Eq. (1.2). The existence of a lower density limit for validity of Eq. (2.1) is obvious. Since the thermal pressure of a

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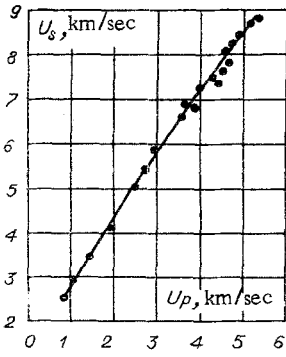


Fig. 1

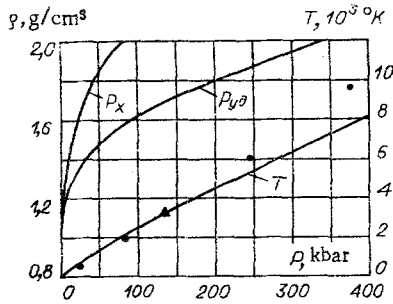


Fig. 2

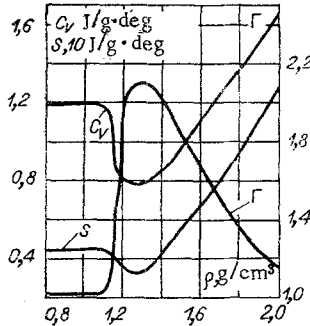


Fig. 3

real gas cannot be less than the pressure of an ideal gas, from the inequality

$$(24.3\rho - 10)T > \rho RT$$

it follows that  $\rho > 0.53 \text{ g/cm}^3$ . Moreover, as will be shown below, Eq. (2.1) gives valid thermal pressure  $P_T$  values for liquid nitrogen at the boiling temperature. [It should be noted now that according to Eq. (2.1)  $P_X(\rho)$  of liquid nitrogen at a density of  $0.82 \text{ g/cm}^3$  is negative and equal to 0.75 kbar, while  $P_X(\rho)$  of gaseous nitrogen at the same density is close to zero, i.e., in fact  $P_X(\rho)$  of nitrogen does depend on temperature also, although weakly.]

Thus, the dependence of thermal pressure on density and temperature proves to be linear over a wide range, which suggests the preservation of this linearity at the higher density and temperature values attained behind a shock-wave front. A linear dependence of pressure on temperature at high densities also follows from Eq. (1.2).

We will consider the conditions under which the expression for pressure behind a shock-wave front (neglecting  $P_0$ )

$$P = \rho_0 U_s U_p \quad (2.2)$$

will coincide with pressure found from Eq. (2.1). We write the shock-wave velocity  $U_s$  as a function of mass velocity  $U_p$  behind the front in the following manner:

$$U_s = S U_p + C, \quad (2.3)$$

where  $S$  and  $C$  are some functions of  $U_p$  [7]. Then from Eqs. (2.2), (2.3) we obtain

$$P = \rho_0 S U_p^2 + \rho_0 C U_p. \quad (2.4)$$

We add and subtract from Eq. (2.2) the second term of Eq. (2.4),

$$P = (\rho_0 U_s U_p - \rho_0 C U_p) + \rho_0 C U_p$$

and rewrite the result,

$$P = \left( 24.3\rho - \frac{24.3\rho C}{U_s} \right) \frac{\rho_0 U_s U_p}{24.3\rho} + \rho_0 C U_p. \quad (2.5)$$

Now comparing Eqs. (2.1) and (2.5), we arrive at the result

$$\frac{24.3\rho C}{U_s} = 10, \quad (2.6)$$

which must be fulfilled along the shock adiabat, if the behavior of the nitrogen behind the shock-wave front can be described by equation of state (2.1). With the aid of the equation for conservation of mass in the shock-wave front,

$$\frac{\rho_0}{\rho} = \frac{U_s - U_p}{U_s} \quad (2.7)$$

and Eq. (2.3), which may be rewritten in differential form, setting  $S$  equal to  $dU_s/dU_p$ , since

$$U_s = \frac{dU_s}{dU_p} U_p + C, \quad (2.8)$$

it is simple to derive from Eq. (2.6) the equation of the shock adiabat in variables  $U_s$  and  $U_p$ , which may be written approximately as

$$U_s = U_p + 1.3 \sqrt{U_p}, \quad (2.9)$$

where the constant of integration of differential equation (2.8) is evaluated from the results of [3]. The shock adiabat constructed from Eq. (2.9) is shown in Fig. 1 together with experimental points [3]. It is

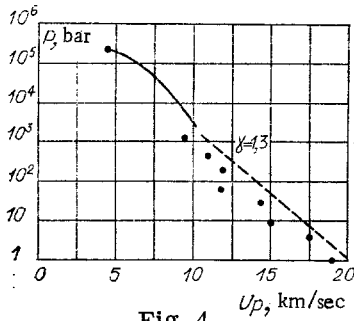


Fig. 4

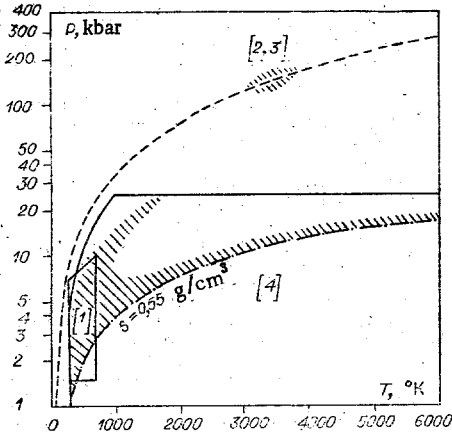


Fig. 5

evident that agreement with experiment is good. Assuming that in the interval between the regions where Eq. (1.2) and Eq. (2.1) are valid the dependence of pressure on temperature in the equation of state remains linear for constant density, from comparison of Eq. (2.5), which we may rewrite as

$$P = (24.3\rho - 10) \frac{\rho_0 U_s U_p}{24.3\rho} + \rho_0 C U_p, \quad (2.10)$$

and equation of state (2.1), it follows that behind a shock-wave front in liquid nitrogen

$$T = \frac{\rho_0 U_s U_p}{24.3\rho}, \quad P_x(\rho) = \rho_0 C U_p. \quad (2.11)$$

The change in temperature with increase in pressure, and consequently, density, along the shock adiabat of liquid nitrogen is shown in Fig. 2. Also shown are the calculated points of [2], denoted by circles, and the calculations of [3], denoted by a triangle.

In the approximation of Eq. (2.9) from Eqs. (2.7)-(2.9) and (2.11) we obtain the dependence of cold pressure on density:

$$P_x(\rho) = 26.9 \left( \frac{\rho}{\rho_0} - 1 \right)^3.$$

This function and the shock adiabat are shown in Fig. 2.

The elastic fraction of the internal energy of a shock-compressed material may be found from the identity

$$dE_x + P_x dV = 0,$$

while the thermal fraction of the internal energy is the difference between  $E_x$  and the total internal energy

$$E = \frac{P + P_0}{2} (V_0 - V) + E_0.$$

The thermal fraction  $E_0$  is then equal to  $C_V T_0$ , where  $C_V$ , the heat capacity of nitrogen at 75°K and a density of 0.82 g/cm<sup>3</sup>, is taken equal to 4R, which leads to agreement of the value of  $C_P/C_V$ , and, consequently, also  $P_t$  [6] with the values presented in [12].

Knowledge of the thermal fraction of the energy and the temperature permits calculation of the nitrogen heat capacity behind the shock-wave front (Fig. 3). An increase in heat capacity at densities above 1.67 g/cm<sup>3</sup> to values greater than 5R may be produced by change in the effective molecular weight of the nitrogen behind the shock-wave front. (In [3], from analysis of data on shock compression at a density of 1.65 g/cm<sup>3</sup> fusion of the nitrogen was proposed.) A sharp decrease in heat capacity at a density near 1.2 g/cm<sup>3</sup> supports the conclusion, also made in [3], of the possibility of crystallization, i.e., freezing of rotational degrees of freedom of the nitrogen molecules behind the shock-wave front. Upon crystallization the nitrogen entropy must also decrease, its value being determined by the second law of thermodynamics with the aid of Eq. (2.1):

$$S = C_V \ln T - 24.3 \ln \rho - \frac{1}{\rho} + S_0. \quad (2.12)$$

It was assumed that  $C_V$  varies with density in the same fashion as along the shock adiabat. In the future  $S_0$  will be taken as zero. The change in nitrogen entropy along the shock adiabat, and also the dependence of the Grüneisen coefficient on density, found from the equation

$$\Gamma(\rho) = \frac{P_T}{\rho E_T},$$

are shown in Fig. 3.

Equation of state (2.1) and Eq. (2.12) were employed to calculate the unidimensional isentropic discharge of nitrogen compressed to 270 kbar by a shock wave. Figure 4 shows the mass velocity as a func-

tion of pressure in the flow as calculated, together with the experimental results of [13]. A certain divergence may be explained by the idealized formulation used in computation, since in experiment the conditions indicated occur only at the initial moment.

### 3. Analysis of Results

The equation of state of dense nitrogen obtained in the study, shown in Fig. 5, was compared with experimental results on static compression of nitrogen to densities of the order of 1 g/cm<sup>3</sup> and pressures of 10 kbar in the temperature range 300-700°K [1], with the calculations of [4], which in the authors' opinion are valid to pressures of 25 kbar and temperatures of 300 to 6000°K, and with results of computing temperature behind a shock-wave front [2, 3]. The dashed line indicates the shock adiabat of liquid nitrogen as calculated from the results of the present study. Regions in which the results of the present study practically coincide with the results of [1-4] are cross-hatched. A density close to 0.55 g/cm<sup>3</sup> is the natural limit of applicability of the equation of state employed in the present calculations.

Thus, the empirical equation of state derived herein not only describes the results of static compression of nitrogen to densities of the order of 1 g/cm<sup>3</sup> well, but also agrees with experimental data on shock compression and isentropic discharge of nitrogen up to densities of the order of 2 g/cm<sup>3</sup>.

### 4. Shock Adiabats of Liquid Argon, Deuterium, and Hydrogen

It develops that the shock adiabats of liquid argon, deuterium, and hydrogen at sufficiently high pressures and temperatures behind a shock-wave front, when initial values may be neglected, as in the case of nitrogen, may be represented in the form

$$U_s = U_p + \text{const} \sqrt{U_p},$$

where the constants for argon, deuterium, and hydrogen, respectively, are equal to 1.8, 1.3, 1.43. This function agrees well with the experimental shock adiabat of liquid argon [14] and practically coincides with shock adiabats of liquid deuterium and hydrogen calculated in [15] for pressures up to 200 kbar. This then permits the assumption that in analogy to nitrogen the "cold" compression pressure of these substances may be described with sufficient accuracy by a third-degree power function of the density.

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