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SHOCK COMPRESSIBILITY OF LIQUID NITROGEN AND SOLID CARBON DIOXIDE

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Experimental investigations of the compressibility of N_2 and CO_2 by static methods pertain to the region of comparatively low pressures and densities. Thus, for N_2 the highest pressures (P = 15,000 atm) and densities ($\rho = 1.1$ g/cm^3) were attained by Bridgman ([1]) under isothermal compression of nitrogen (T = 338° K). More detailed investigations of the equations of state of these substances were carried out at still lower pressures (see the bibliography in ([2])).

The purpose of the present work was to attain pressures of the order of hundreds of thousands of atmospheres and densities of $\sim 2 \div 3$ g/cm^3 in substances that constitute the principal part of the explosion products formed in the detonation of condensed explosives.

The only method that ensures the attainment of such high pressures is compression of a substance in strong shock waves (see, for example, ([3], [4])). Single shock compression leads to high densities if, before compression, the substance is already in a sufficiently dense state. For substances that under ordinary conditions are gases, this condition is most easily satisfied by taking them in the condensed phase at low temperature. Such a study of liquefied Ar and O_2 was carried out earlier ([5]) by the method of pulsed radiography up to pressures of $\sim$ 80,000 atm. From the radiographs the velocity of the shock wave and the density of the substance behind the wave front were determined. These two quantities are sufficient to calculate, from the conservation laws, the remaining parameters determining the state of the compressed substance.

In our work, by the method of braking plates accelerated to high velocities ([3]), substantially higher pressures ($\sim$ 0.5 million atm) were obtained in CO_2 and N_2. With a known intensity of the shock wave in the shield from which the wave passes into the substance under study, determination of the state of the substance requires measurement in it of only one velocity of the shock wave.

Experimental arrangement and results

In the pressure range $2 \cdot 10^5$ atm, plane shock waves in the substances under study were produced by a charge of explosive separated from the substance by a metallic shield.

At higher pressures, shock waves in the shields covering the substance under study were produced by the impact of plates accelerated by the explosion products. The intensity of the wave in Al and Cu shields, whose shock adiabats are known ([6]), was determined in preliminary experiments by measuring the wave velocities. The latter were recorded by an electrical-contact method ([7]).

During the measurements, liquid nitrogen at $T_{boil} = 77.4°$ K ($\rho_0 = 0.808$ g/cm^3) was in the inner cavity of a metal cup with double walls separated by an air gap. To avoid boiling, the inner cup was cooled from outside with liquid nitrogen, which was poured into the gap. When boiling in the inner cup ceased, the nitrogen from the gap-

was quickly removed. After this the experiment was carried out for 1-3 sec. It had been established beforehand that, for 5–10 sec from the moment of removal of nitrogen from the gap, under our conditions practically no boiling occurs in the inner beaker.

In experiments with solid carbon dioxide ($T_{isp} = 196°$ K, $\rho_0 = 1.54$ g/cm^3), no special cooling measures were taken. As the specimen evaporated, the panel with rigid contacts, recessed into the CO_2, was moved toward the screen by special springs. The experiment was carried out at the moment of closure of the control contact, when the middle of the measurement base was at the prescribed distance from the screen.

Table 1

u_e^*, km/sec	N_2				CO_2			
	D, km/sec	u, km/sec	P, kbar	ρ, g/cm^3	D, km/sec	u, km/sec	P, kbar	ρ, g/cm^3
0.69	3.14	1.17	29.6	1.29	3.57	1.03	53.4	2.04
0.845**	3.74	1.57	47.4	1.39	–	–	–	–
1.55	5.00	2.50	101	1.62	5.38	2.14	167	2.40
2.80	7.45	4.27	257	1.90	7.71	3.68	412	2.77
3.68	9.05	5.52	404	2.07	9.05	4.79	631	3.10

* As a check showed, the presence of a gap in the screen in experiments with N_2, within the limits of error, does not change the intensity of the shock wave in the screen.
** Screen of Cu. In all other cases the screen was of Al.

The results of measuring the wave velocities D and the mass velocities u, pressures, and densities determined from them are given in Table 1. Each value of D in Table 1 is the result of averaging 4-12 independent measurements. The root-mean-square deviation from the mean is 1-2%.

In determining the pressure and mass velocity from the measured wave velocities, it was assumed that the release isentrope of the screen material coincides with the mirror reflection of the shock adiabats. A check at the highest pressures showed that the inaccuracy allowed thereby lies within the experimental errors. The shock adiabats of Al and Cu were taken from work ([6]).

At the high densities that are realized under our conditions, it may evidently be assumed that the molecules spend the overwhelming part of the time near certain equilibrium positions in volumes bounded by neighboring molecules. It is precisely from such premises, without counting additional simplifications, that the free-volume theory of Lennard-Jones and Devonshire ([8]) proceeds. Therefore a comparison was made of the experimental data obtained with calculations according to the free-volume theory in the form in which they are presented in work ([9]). Using the calculations given in ([9]), we constructed the shock adiabats of N_2 and CO_2. In doing so, a large discrepancy was found between the calculated shock adiabats and the experimental points (Figs. 1 and 2). By changing the constants entering into the power-law pair-interaction potential

$$\Phi(r) = \frac{\varepsilon_m}{s/6-1}\left(\frac{s}{6}\right)^{\frac{s}{s-6}}\left[\left(\frac{r_0}{r}\right)^s - \left(\frac{r_0}{r}\right)^6\right], \tag{1}$$

while keeping $s = 12$, for which the calculations ([9]) were performed, it is difficult to achieve good agreement of the calculated shock adiabat with all the experimental points.

Therefore we carried out numerical calculations for $s = 9$ and compiled tables of the integrals G, g_L, g_M as functions of v/r_0^3 and kT/ε_m (v is the volume per particle), analogously to the way this was done in ([9]).

These integrals, for known r_0 and ε_m, give the internal energy E and pressure P as functions of v/r_0^3 and kT/ε_m:

$$E = E_{\text{id}}(T) + 12\varepsilon_m\left[\left(1.04 + 2\frac{g_L}{G}\right)\left(\frac{v_0}{v}\right)^3 - 1.5\left(1.2 + 2\frac{g_M}{G}\right)\left(\frac{v_0}{v}\right)^2\right]; \tag{2}$$

$$P = \frac{kT}{v} + \frac{36\varepsilon_m}{v}\left[\left(1.04 + 2\frac{g_L}{G}\right)\left(\frac{v_0}{v}\right)^3 - \left(1.2 + 2\frac{g_M}{G}\right)\left(\frac{v_0}{v}\right)^2\right], \tag{3}$$

where $v_0 = r_0^3$.

In calculating $E_{\text{id}}(T)$ for comparatively high temperatures on the shock adiabat it is necessary, along with translational and rotational motion, to take into account excitation of the vibrational degrees of freedom of the molecules.

(Figure: Fig. 1. Shock adiabat of N_2. 1 –from calculation results (9), $s = 12$, $\varepsilon_m/k = 91.5^\circ$ K, $r_0 = 3.68$ Å; 2 –calculation for $s = 9$, $\varepsilon_m/k = 91.5^\circ$ K, $r_0 = 3.73$ Å; points –experiment)

Fig. 1. Shock adiabat of N_2.
1 –from calculation results (9), $s = 12$, $\varepsilon_m/k = 91.5^\circ$ K, $r_0 = 3.68$ Å; 2 –calculation for $s = 9$, $\varepsilon_m/k = 91.5^\circ$ K, $r_0 = 3.73$ Å; points –experiment.

(Figure: Fig. 2. Shock adiabat of CO_2. 1 –from calculation results (9), $s = 12$, $\varepsilon_m/k = 190°$ K, $r_0 = 3.996$ Å; 2 –calculation for $s = 9$, $\varepsilon_m/k = 290°$ K, $r_0 = 3.78$ Å; points –experiment)

Fig. 2. Shock adiabat of CO_2.
1 –from calculation results (9), $s = 12$, $\varepsilon_m/k = 190°$ K, $r_0 = 3.996$ Å; 2 –calculation for $s = 9$, $\varepsilon_m/k = 290°$ K, $r_0 = 3.78$ Å; points –experiment.

$$E_{\text{id}}(T) = \frac{5}{2}kT + \sum_i \frac{k\theta_i}{e^{\theta_i/T} - 1}, \tag{4}$$

θ_i corresponds to different types of vibrations. For N_2 the sum contains only one term, where $\theta = 3340°$ K, while in the case of CO_2 the sum consists of four terms: $\theta_i = 954;\ 954;\ 1890$ and $3360°$ K.

The shock adiabat is determined by the law of conservation of energy

$$E = \frac{1}{2}(P + P_0)(v_0 - v) + E_0. \tag{5}$$

r_0 was determined from the density of the crystals ρ_{0k} of N_2 and CO_2, and ε_m from the condition of the best agreement between the calculated shock adiabat and the experimental points. The values of these constants are given in Table 2. The values of E_0, entering into equation (5), are also given there.

Table 2

Substance	ρ_{0k}, g/cm^3	$E_0 \cdot 10^{-9}$, erg/g	r_0, Å	$\frac{\varepsilon_m}{k}$, °K
N_2	1.03	−1.2	3.73	91.5
CO_2	1.56	−0.63	3.78	290

Equation (5) was solved graphically. At a fixed density, the temperature at which this equality was satisfied was found. The shock adiabats calculated in this way describe the experimental data rather well (Figs. 1 and 2). Table 3 gives the results of calculating the temperatures on the shock adiabats.

Table 3

	N_2	N_2	N_2	N_2	N_2	CO_2	CO_2	CO_2	CO_2	CO_2
$P \cdot 10^{-9}$, bar	6.36	24.2	83.6	245	595	16.0	54	162	394	1000
ρ, g/cm^3	1.056	1.33	1.61	1.87	2.14	1.62	2.02	2.43	2.83	3.22

	N_2	N_2	N_2	N_2	N_2	CO_2	CO_2	CO_2	CO_2	CO_2
$T \cdot 10^{-3}$, °K	0.16	0.61	2.0	6.09	15.5	0.695	0.950	2.14	5.0	13.2

As is seen from the table, a twofold increase in density under shock compression leads to a strong rise in temperature—to 10,000-15,000°.

In formulas (2) and (3) one can separate out the part that does not depend on temperature

$$\left(\frac{g_L}{G},\ \frac{g_M}{G} \to 0 \text{ as } T \to 0\right).$$

This part of the pressure and energy arises as a consequence of the repulsion (or attraction) of molecules in the complete absence of thermal motion; i.e., in the present case one can, just as in the theory of small oscillations, separate out the "cold" components of P and E ([6]).

Proceeding from this, it is interesting to note that at the temperatures (~4000°K) realized in the detonation of condensed high explosives ([10], [11]), the thermal pressure, i.e., the part of the pressure due to thermal motion, amounts to ~40% of the total pressure, and the thermal energy to ~70-80%. From these results one may conclude that the thermal motion of molecules plays an essential role when considering the equation of state of explosion products.

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Note: Figure translations are in progress. See original paper for figures.