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## Abstract

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# DETERMINATION OF THE TEMPERATURES OF ORGANIC SUBSTANCES IN SHOCK WAVES

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To study the state of matter at high pressures, data obtained in experiments with shock waves are often used. The most fully developed and widely applied are various methods for recording the kinematic characteristics of shock waves —the propagation velocity $D$ and the mass flux $u$—from which, by means of the conservation laws of mass and momentum, one can readily pass to such parameters of the state of the compressed substance as the pressure $P$ and the specific volume $v$. The shock adiabats of many substances have been investigated experimentally, and for most of the others their course can be predicted with acceptable accuracy ([1,2]).

Temperatures $T$ of matter in shock waves have been measured much less often (one may cite only the works ([3–6])), although without knowing them a comprehensive analysis of the possible form of the equation of state of the compressed substance, involving only the dependences $P(v)$, cannot be carried out.

The measurement of the temperatures of shock-compressed substances has a number of special features associated with the fact that, in a real experiment, the times during which constant values of the state parameters are maintained are of the order of $10^{-6}$ sec. This does not allow contact methods of temperature measurement to be used because of their inertia. An additional complication in the case of thermocouples is, moreover, the change in thermoe.m.f. at high pressures ([7]). Optical methods, which are advantageously distinguished by their lack of inertia, are especially effective in measuring the temperatures of homogeneous substances that, before compression, possessed sufficiently high transparency. In this case, through the layer of still uncompressed substance, the spectral brightnesses of the shock-front luminosity are recorded; taking into account the extremely small thickness of the shock transition in liquids and single crystals, these brightnesses are usually associated with the temperatures of the substance behind the shock front.

In the present communication the results are described of measurements of the

Fig. 1

Figure 1: Fig. 1

temperatures of shock-compressed organic liquids, carried out by an electro-optical method. The specific experimental arrangement is given in Fig. 1, and the necessary explanations for it are provided in the text below. The luminosity of the shock wave in the liquid under study was recorded by an FEU-28 photomultiplier, the current of which was recorded on an OK-17M oscilloscope with a linear-sweep region increased to 35 mm (instead of 18 mm on the standard instruments). Time marks at intervals of 1 $\mu$sec were given on the second beam of the oscilloscope.

Between the sample under study and the photomultiplier there were a diaphragm 3 for cutting off the luminosity of the peripheral regions of the sample covered by the lateral rarefaction wave, a two-objective system 4–5 for focusing the luminosity of the central part of sample 2 onto the photocathode of the FEU-28, and a KS-19 light filter, which transmitted radiation in the region $\lambda > 700$ m$\mu$.

If necessary, neutral light filters of various densities were placed in front of the input lens; this made it possible to measure temperatures, at constant operating regimes of the photomultiplier and oscilloscope, over a wide range of brightnesses of the glow of the liquids under study. Synchronization of the oscilloscope sweep with the moment at which the shock wave entered the liquid was achieved by setting the charge of the spark sensor 6. The time resolution of the glow recording was 0.1-0.2 $\mu$sec. The design and dimensions of the charges 1, which generated shock waves with a plane front in the liquids, ensured a pressure drop behind the front during the first microsecond of not more than 5%. The scatter of pressure in identical experiments did not exceed 1%.

**Fig. 1**

The shock adiabats of the liquids studied were represented in the form

$$D = c_0 + 2u - 0.1u^2/c_0,$$

where $D$ is the shock-wave velocity, $u$ is the velocity of the substance behind the shock front, and $c_0$ is the speed of sound in the initial state. The last equation makes it possible, with accuracy sufficient for the purposes of the present investigation, to generalize the experimental material available in the literature on shock compression of organic liquids (as applied to the substances used in the present work, see ([8],[9])) and eliminates the need to carry out additional measurements.

**Fig. 2**

Fig. 2

Figure 2: Fig. 2

A typical oscillogram of the recording of the brightness of the glow of the shock front as the wave passes through the sample is shown in Fig. 2a. Saturation of the brightness (formation of an equilibrium radiating layer) occurred in about 0.2 $\mu$sec; afterward a slow decrease was observed, caused by the decrease in pressure at the wave front as it passed through the sample. Measurements of brightness temperatures were carried out at the maximum of the glow. The values obtained, which are the result of averaging 3–5 experiments with a root-mean-square deviation of less than 100°K, are given in Table 1.

The lower limit of the temperatures measured was limited by two factors: the level of light interference from side phenomena associated with the scattering of the explosion products of the active charge, and the transparency of the substance behind the shock-wave front. To reduce the level of interference, the active charge was placed in a dark box, which was destroyed some time after the detonation of the active charge had ended. This time was quite sufficient for the shock wave to pass through the cuvette with the liquid under investigation. The transparency of the substance behind the shock-wave front affects the minimum measurable temperature through the possibility, in a real experiment, of producing a layer of compressed substance with definite state parameters and radiating in equilibrium, since only for such a layer do the concept and measurement of temperature have meaning.

**Table 1**

| Substance | $P$, kbar | $T_{\text{expt}}$, °K | $T_{\text{calc}}$, °K |
|---|---:|---:|---:|
| Toluene | 150 | 1450 | 1300 |
| Methanol | 140 | 1400 | 1500 |
| Hexane | 120 | 1200 | 1200 |
| Carbon tetrachloride | 85 | 1400 | 1320 |
| Carbon tetrachloride | 110 | 1600 | 1650 |
| Carbon tetrachloride | 123 | 1900 | 1830 |
| Carbon tetrachloride | 162 | 2400 | 2370 |
| Carbon tetrachloride | 203 | 2900 | 2940 |

| Substance | $P$, kbar | $T_{\text{expt}}$, °K | $T_{\text{calc}}$, °K |
|---|---|---|---|
| Solution of carbon tetrachloride with benzene 63/37 | 115 | 1500 | 1580 |
| Solution of carbon tetrachloride with benzene 63/37 | 120 | 1600 | 1650 |
| Solution of carbon tetrachloride with benzene 63/37 | 145 | 1900 | 1950 |
| Solution of carbon tetrachloride with benzene 63/37 | 179 | 2300 | 2350 |
| Solution of carbon tetrachloride with benzene 63/37 | 184 | 2350 | 2400 |

The upper limit of the temperatures attained in shock compression was determined by the detonation pressures of the active charges and by the chosen scheme for forming the shock wave. The reasons listed in the last two paragraphs led to the fact that, for most of the liquids investigated, it was not possible to record the temperature-pressure dependence of the substance under shock compression.

The measured temperatures are brightness temperatures $T_{\text{b}}$, and in order to pass from them to the true temperatures $T_{\text{t}}$ it is necessary to know the emissivity of the compressed substance $\varepsilon_\lambda$: $\frac{1}{T_{\text{b}}} - \frac{1}{T_{\text{t}}} = \frac{\lambda}{C_2} \ln \varepsilon_\lambda$, where $C_2 = 1.438°\text{K} \cdot \text{cm}$, and $\lambda$ is the wavelength of the radiation. For a body radiating in equilibrium, the quantity $\varepsilon_\lambda$ is related to the transmission and reflection coefficients $\tau_\lambda$ and $r_\lambda$ by the relation $\varepsilon_\lambda = 1 - \tau_\lambda - r_\lambda$.

The reflectivity of shock fronts $r_\lambda$ at pressures in the wave of 100-200 kbar, according to the data presented in ([10]), does not exceed 0.1. The transparency $\tau_\lambda$ of organic liquids compressed by a shock wave to the pressures at which the measurements were made is also small, as is indicated by the rapid increase in the brightness of the glow as the shock wave passes through the sample (Fig. 2a), and also by the results of experiments in which, following the first shock wave, a second wave propagated through the liquid with a somewhat higher temperature at the front. The brightness of the glow during the overtaking of the first wave by the second increased by a sharp jump over times of 0.1-0.2 $\mu$sec (see Fig. 2b), which are close to the limit of the time resolution of the apparatus. If the substance behind the first shock wave were transparent, the brightness would increase smoothly as the shock fronts approached one another.

Taking $\varepsilon_\lambda = 0.8$, we find, for $T_\mathrm{b} = 2000°\mathrm{K}$ and $\lambda = 700\,m\mu$, the difference between $T_\mathrm{b}$ and $T_\mathrm{t}$ to be approximately 50°K, i.e., less than the possible error of the measurements. For this reason, when comparing the experimental values of the shock-compression temperatures with the results of calculation, the difference between brightness and true temperatures may be neglected.

The measured temperatures of shock-compressed organic substances can be calculated with good accuracy by using the equation of state of a molecular crystal. According to this model, the intramolecular characteristic frequencies (temperatures) do not depend on the degree of compression. Then the partition function of the substance may be represented in the form

$$\ln K(T) = E_0(v) - 9N\frac{T^3}{\theta_D}\int_0^{\theta_D/T} \xi^2 \ln(1-e^{-\xi})\,d\xi + N\ln j(T),$$

where $E_0$ and $\theta_D$ are the lowest possible energy and the Debye temperature of intermolecular interaction; $\ln j(T)$ is the contribution of intramolecular degrees of freedom, whose characteristic frequencies remain constant under compression.

The expressions for the pressure and internal energy are written as

$$P = P_x(v) + \frac{3R\Gamma(v)}{Mv}\int_T D\left(\frac{T}{\theta_D}\right)dT; \qquad E = E_x(v) + \int_T c_v(v,T)\,dT,$$

where $D(T/\theta_D)$ is the Debye function; $\Gamma(v) = \partial\ln\theta_D/\partial\ln v$ is the Grüneisen coefficient.

At temperatures above 100° K, the expression for the equation of state and the internal energy can be reduced to the form

$$P = P_x(v) + \frac{3R\Gamma(v)}{MV}T; \qquad E = E_x + \int_T c_v(T)\,dT.$$

The expression for the caloric equation of state and the internal energy of molecular liquids will be the same as for crystals, although in the expressions for the entropy and free energy there appears an additional term associated with the lesser degree of order.

The temperature at the shock front is found by the simultaneous solution of the energy-conservation equations and $P_x(v)$

$$\Delta E_T = \int_{T_0}^{T} c_v\, dT = \frac{1}{2}P(v_0 - v) - \int_{v_0}^{v} P_x\, dv; \qquad P = P_x + \frac{3R\Gamma(v)}{MV}T,$$

where $P$ and $T$ are the pressure and temperature at the shock front. The solution of these equations must satisfy the thermodynamic identity

$$(\partial P/\partial T)_v(\partial T/\partial v)_p(\partial v/\partial P)_T = -1.$$

In the course of the calculation, simultaneously with the temperature, the zero isotherm and the Grüneisen coefficient $\Gamma(v)$ are found; these determine the equation of state within the framework of the selected model.

The values of the temperatures of organic liquids in shock waves calculated in this way are given in Table 1.

The good agreement between the results of the calculation and the experimental values of the shock-compression temperatures is, in our view, a weighty argument in favor of the validity of the assumption that the characteristic temperatures of intramolecular interaction in organic liquids remain unchanged upon compression up to 200 kbar, and possibly to still higher pressures.

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