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1. A feature of the investigation of the properties of metals by dynamic methods is that they make it possible to determine, over a broad range of the parameters, only the pressure p , the specific volume v , and the internal energy E as a function of pressure and volume. The experimental information thus obtained turns out to be inadequate for constructing the equation of state (ES) owing to the absence of such important thermodynamic characteristics as the temperature T and entropy of the shock-compressed material. The experimental measurement of these quantities together with the other shock-compression parameters presents serious difficulties since with metals it is not possible to employ optical recording techniques.

However, the entropy and temperature on the shock adiabats can be determined from the end-state parameters of the metal on isentropic expansion. Zel'dovich [1] was the first to draw attention to the feasibility of this method of determining the temperature and entropy in shock waves.

For shock waves with pressures of hundreds of GPa, the authors of [2] proposed, and demonstrated experimentally on lead, a method of determining the entropy on the Hugoniot adiabat based on investigating the process of vaporization of metals in unloading waves. In [2] the vaporization effects were revealed by measuring the rate of isentropic expansion into air with an initial pressure $p_0 = 10^5$ Pa of lead specimens compressed by shock waves of varying intensity. The sharp break observed in the dependence of the rate of expansion w of lead into air on the mass velocity u in the shock wave was associated with the unloading pressure at which vaporization began, which defined for one of the isentropes its point of intersection with the liquid-vapor equilibrium line, whose parameters, including entropy, were assumed to be known. The value of the mass velocity u corresponding to the sharp break on the $w(u)$ curve determines the pressure and degree of compression on the Hugoniot. In view of the isentropicity of the unloading process, the entropy at the point of intersection of the isentrope and the phase boundary is equal to the entropy in the shock-compressed state.

In our research we experimentally determined the rates of expansion into air of five metals (Al, Mg, Cu, Sn, and Cd) with different bond energies and boiling points. In this series of metals Cd has the lowest bond energy ($Q_b = 1$ kJ/g) and Al the greatest, 12 times the bond energy of Cd. For three metals (Al, Mg, Cu) we obtained smooth monotonic $w(u)$ curves, which indicated the passage of the unloading curves through states of the condensed metal. For Cd and Sn the break on the $w(u)$ curve revealed "critical" shock pressures above which the expansion process led to partial vaporization of the metal.

2. The vaporization effects were detected in the same way as in [2], by measuring the rate of isentropic expansion into air at normal pressure of metal specimens compressed by shock waves of varying intensity. From the results of the experiments we determined the dependence of the unloading velocity w on the mass velocity u in the shock wave.

Let us consider the schematic p - v diagrams (Fig. 1) and the states attained in the experiment, taking into account the fact that for certain unloading isentropes the end states lie inside the two-phase liquid-vapor region (the fusion region is not shown in Fig. 1). In Fig. 1: 1 is the shock adiabat, 2 are the unloading isentropes (the dashed lines correspond to metastable isentropes), 3 is the end-state curve for unloading into air, 4 is the boundary of the two-phase liquid-vapor region.

The change in isentropic compressibility on crossing the phase equilibrium boundary is equal to [2]

*Deceased.

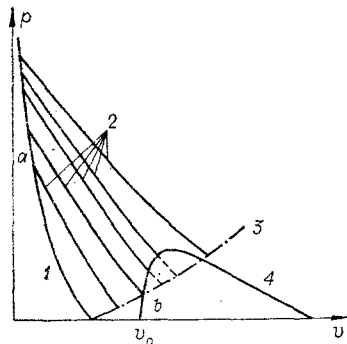


Fig. 1

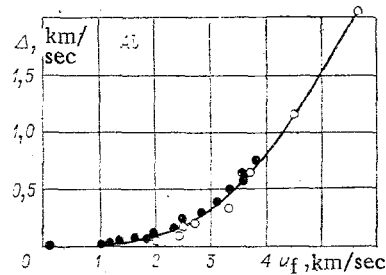


Fig. 2

$$\left(\frac{\partial v_2}{\partial p}\right)_{s_2} - \left(\frac{\partial v_1}{\partial p}\right)_{s_1} = -\frac{T}{C_{p1}} \left(\frac{dS_1}{dp}\right)^2. \quad (2.1)$$

In (2.1) the total derivatives relate to the phase equilibrium line, the subscript 1 relates to the liquid phase, and the subscript 2 to the region of phase coexistence. The change of mass velocity on the isentrope is expressed in terms of the derivatives in (2.1) by the relation

$$(\partial u / \partial p)_s = \sqrt{-(\partial v / \partial p)_s}. \quad (2.2)$$

From a comparison of (2.1) and (2.2) it follows that entry of the isentrope into the two-phase region from the liquid (evaporation) or gas (condensation) phase causes a further increase in the velocity $w = u_f + u(p \approx 0)$, where u_f is the mass velocity at the shock front. The dependence of the unloading velocity in the end states on the parameters of the initial state in the compression wave will be monotonic for expansion of the metal along metastable adiabatics (dashed lines in Fig. 1) and will have two breaks for equilibrium expansion. Of these the more conspicuous should be that corresponding to the beginning of vaporization, owing to the substantial difference in compressibility in the liquid and gaseous states. Thus, the presence of a break on the experimental $w(u)$ curve makes it possible to detect the vaporization of the metal. The coordinates of the break make it possible to isolate in the experiments the isentrope ab (see Fig. 1), whose end state lies on the equilibrium line. The value w_b from the known shock adiabat for air determines the air pressure p_b , which, by virtue of the condition of flow continuity at the contact boundary, coincides with the pressure of the expanding metal. In this case the pressure and degree of compression in the starting a -state of the isentrope are found from the value u_a at the break point on the $w(u)$ curve.

A detailed description of the experimental technique was given in [2]. The essence of the experiments consisted in creating powerful shock waves in specimens of the metals investigated by means of calibrated explosive devices, with subsequent recording of the expansion velocity on arrival of the shock wave at the metal-air interface.

In using the photochronographic method of recording the expansion velocity, we experimentally determined not the velocity of the disintegrating metal, as in [2], but the velocity of the air shock. Conversion to mass velocities presents no difficulties, since the dynamic compressibility of air is well known [3]. This made it possible to improve to some extent the accuracy and reliability of the results.

The results of the experiments to determine the expansion velocities are summarized in Table 1, which also gives the initial and end-state parameters of the specimens investigated. The pressures and mass velocities corresponding to the initial states in the shock front were found from the known parameters of the explosive devices and the Hugoniot adiabatics of the investigated metals published in [4]. The end pressures, corresponding to unloading into air, were determined from the measured values of w or D and the dynamic adiabat for air [3]. Table 1 also gives the difference $\Delta = w - 2u$ characterizing the deviations from the "rule of two." The values of w presented in Table 1 were obtained by averaging 4-7 experiments. As may be seen from Table 1, the set of explosive devices employed made it possible to determine the unloading velocities over a very broad interval of pressures: $p \approx 30-200$ GPa.

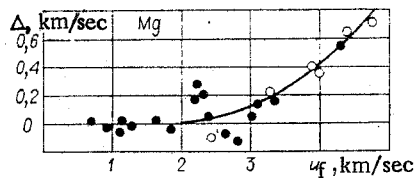


Fig. 3

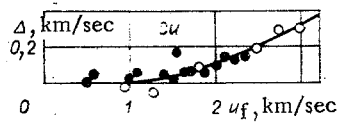


Fig. 4

The experimental data obtained are illustrated in Figs. 2-6, which also reproduce the points ● corresponding to individual experiments [5]. Attention is drawn to the difference in the behavior of the $\Delta(u)$ curves of two groups of metals: (I) Al, Mg, Cu; (II) Cd, Sn. For the first group the experimental results are described by a single ascending curve over the entire pressure interval investigated. On the $\Delta(u)$ curves for Cd and Sn it is possible to distinguish two segments with different slopes, the break being most apparent on the Cd curve.

The smooth increase in expansion velocity with increase in shock wave intensity in the compressed states of Al, Mg, and Cu indicates that on unloading into air these metals remain in the condensed state. Calculations of the entropies of the condensed phase, based on semi-empirical ES of Al, Mg, and Cu [6], also showed that the shock wave pressure amplitudes achieved in the experiments were insufficient for transition to the two-phase region on unloading.

The breaks on the $\Delta(u)$ curves for Cd and Sn indicate, as suggested above, the onset of vaporization of the specimens in the unloading wave. The coordinates of the breaks correspond to the isentropes with the parameters of the starting α - (on the shock adiabats) and end b -states (on unloading into air) presented in Table 2.

3. To determine the temperature T_b from the given values of p_b on the equilibrium line we use the known (see, for example, [7, 8]) relation between the saturated vapor pressure and

TABLE 1

State on shock adiabat		State on unloading into air			State on shock adiabat		State on unloading into air		
u , km/sec	p , GPa	w , km/sec	p , MPa	Δ , km/sec	u , km/sec	p , GPa	w , km/sec	p , MPa	Δ , km/sec
Aluminum					Lead				
2,02	44	4,06	21,6	0,02	1,47	52	3,05	13,5	0,11
2,47	58	5,02	33	0,08	2,02	83	4,25	24	0,21
2,52	60	5,20	35,5	0,16	2,53	118	5,40	38	0,34
2,72	67	5,62	41	0,18	2,74	134	5,89	45	0,41
3,33	89	6,98	63	0,32	2,98	153	6,45	54	0,49
3,72	105	8,08	84	0,64	3,08	161	6,71	58,6	0,55
4,55	142	10,33*	139	1,23	3,20	171	7,10	65	0,70
5,67	200	13,40*	234	2,06	3,33	183	7,47	72	0,81
					3,48	196	7,93	81	0,97
Magnesium					Cadmium				
2,46	32	4,85	31	-0,07	1,39	58	2,95	11,7	0,17
3,27	49	6,77	60	0,23	1,46	62	3,17	13,5	0,25
3,90	64	8,20	87	0,40	1,90	92	4,09	22,2	0,29
3,99	66	8,36	90	0,38	1,95	96	4,18	23,2	0,28
4,40	76	9,45	115	0,65	2,33	126	5,02	33,1	0,36
4,78	87	10,28	137	0,72	2,58	148	5,83	44,7	0,67
Copper					2,62	152	6,04	47,9	0,80
0,95	45	1,88	5	-0,02	2,90	179	6,92	62,1	1,12
1,27	66	2,50	8,5	-0,04					
1,75	102	3,58	17	0,08					
2,40	161	5,02	34	0,22					
2,72	194	5,73	44	0,29					
2,95	219	6,21	51	0,31					

*The measurements were made by M. I. Brazhnik. Details of similar measurements at high velocities were given in (18).

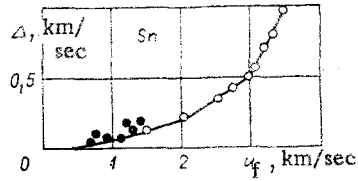


Fig. 5

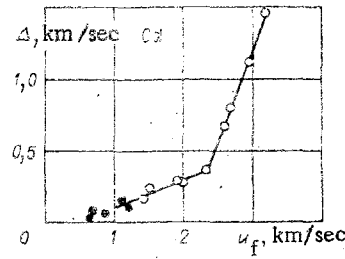


Fig. 6

and temperature

$$\ln p = A(1 - T_e/T), \quad (3.1)$$

where T_e is the boiling point. The temperature found from (3.1) determined the entropy*:

$$S_b = S_e + C_{pl} \ln(T/T_e) - \alpha v p, \quad (3.2)$$

where

$$S_e = S(T_e); \quad \alpha = (1/v)(dv/dp).$$

The last term in (3.2) is small and was not taken into account. The specific heat C_{pl} was assumed to be constant.

From the temperature we also determined the density of the metals in the end states [9]: $\rho_{Cd} = 8.02-1.1 \cdot 10^{-3} (t - 320)$, $\rho_{Sn} = 7.01-7.4 \cdot 10^{-4} (t - 232)$, $\rho_{pb} = 10.71-1.39 \cdot 10^{-3} (t - 327)$ (t, °C).

The characteristics on the isobars $p = 10^5$ Pa (see [10]) and the results of computing T, S, and ρ in the end states for Cd and Sn are presented in the middle and right-hand parts of Table 2.

The accuracy of determination of the entropy of the liquid metal from (3.2) was checked by calculations from the gas phase side. In this case its value on the isobars will be equal to the difference between the entropy of the gas on the equilibrium line and the saturated vapor entropy jump

$$S_l = S_g - \Delta S_{ev}. \quad (3.3)$$

In accordance with [8] it was assumed that for metals the dependence of the reduced heat of vaporization on reduced temperature has the single form:

$$\frac{\Delta H_{ev}}{RT_{cr}} = \frac{\Delta S_{ev}}{R} \frac{T}{T_{cr}} = c \left(1 - \frac{T}{T_{cr}}\right)^d. \quad (3.4)$$

The constants c and d for Cd were found from the values of ΔH_{ev} at the boiling and melting points. For Sn the dependence $\Delta H_{ev}(T)$ from [9] is "wavelike" on the temperature interval $T_m - T_e$; accordingly, the values of c and d were determined on the second descending branch at $T = 0.275T_{cr}$ and $T = 0.375T_{cr}$. The critical temperatures of Cd and Sn have been estimated by many authors and the results are to be found in [11, 12]. On the basis of these estimates it was assumed that for Cd $T_{cr} = 2700^\circ\text{K}$ and for Sn $T_{cr} = 8000^\circ\text{K}$. With these values of the

*The entropy under normal conditions is always taken as the reference point.

TABLE 2

Metal	Parameters on shock adiabat			Characteristics on isobar $p = 10^5$ Pa				End states on unloading					
	u , km/sec	p , GPa	ρ , g/cm ³	T_e , °K	S_e , J/g·°K	C_{pl} , J/g·°K	A	w_b , km/sec	p_b , MPa	T_b , °K	ρ_b , g/cm ³	S_b , J/g·°K	S_b' , J/g·°K
Cd	2.32	124	13.74	1040	0.410	0.264	11.52	5.0	32.8	2090	6.37	0.593	0.602
Sn	3.04	158	12.69	2786	0.663	0.241	12.376	6.58	56.5	5890	3.70	0.835	0.822
Pb	2.20	133	19.34	2023	0.304	0.157	10.57	4.80	33	4000	6.40	0.41*	—

*Refined value according to [17] with allowance for data of [19].

TABLE 3

Metal	ρ_0 , g/cm ³	C_V , J/g·°K	γ_0	β_0 , erg/g·°K	ΔS_m , J/g·°K	T_m , °K	S_α , J/g·°K	T_α , °K
Cd	8,64	0,222	2,22	60	0,093	1640	0,656	5 830
Sn	7,28	0,210	2,01	150	0,117	800	0,829	10 040
Pb	11,34	0,120	2,64	144	0,038	1730	0,422	8 530

critical temperatures the constants in (3.4) are equal to

$$\text{Cd: } c = 4.81, \quad d = 0.165;$$

$$\text{Sn: } c = 4.50, \quad d = 0.026.$$

The entropy of the monatomic ideal gas S_g was taken to be the sum of two components, characterizing the translational motion of the atoms S_{TR} and their electronic state S_{el} . The developed form of the individual entropy components was taken from [8], and the energy levels needed to find S_{el} and their statistical weights were taken from [13].

The values of S_b thus calculated are given in the last column of Table 2. Clearly, the calculations of the entropy on the equilibrium line by the two above methods gives only slightly different results. The values obtained determined the shock compression entropy of Cd and Sn at pressures of 124 and 158 GPa respectively.

4. It is interesting to compare the entropies obtained and the shock-compression entropies calculated on the following assumptions: the lattice heat capacity is constant and equal to $C_V = 3R/\mu$, the electronic heat capacity $C_{el} = \beta_0(v/v_0)^{1/2}T$ [14], the Grüneisen ratio $\gamma = \gamma_0(v/v_0)$ [15]. The entropy jump ΔS_m for shock melting was taken [16] to be the same as at $p = 10^5$ Pa, and the decrease in temperature due to melting was taken into account by means of the relation $\Delta T_m = (\Delta S_m/C_V)T_m(p_m)$, where T_m is the shock melting temperature, which is related to the pressure by Simon's equation. The calculation of T_α and S_α with the subsequent introduction of the corrections ΔS_m and ΔT_m was carried out using the known expressions [2, 15]

$$\frac{dS}{du} = \frac{u^2 D'_u}{DT}; \quad (4.1)$$

$$\frac{dS}{dT} = C_V \left(\frac{1}{T} + \frac{\gamma}{v} \frac{dv}{dT} \right). \quad (4.2)$$

The values of C_V , ρ_0 , γ_0 , ΔS_m and T_m are presented in Table 3, together with the calculated entropies and temperatures of shock compression of Cd and Sn at their "critical" pressures $p_\alpha(\text{Cd}) = 124$ GPa and $p_\alpha(\text{Sn}) = 158$ GPa.

The chosen method of calculating the thermodynamic parameters on the shock adiabats was checked for lead. The parameters, taken from [2], of the initial and end states of the isolated isentrope of Pb are given in the last row of Table 2. As may be seen from Table 3, the calculation of the entropy and temperature from Eqs. (4.1), (4.2) led to more or less similar results. Moreover, these parameters were calculated at other pressures on the shock adiabatic of Pb, and the results were compared with calculations based on the complex interpolation ES of Pb [17].

The results of the independent calculations, presented in Table 4, show good agreement.

Our analysis and, in particular, the similarity of the calculated (Table 3) and experimental (Table 2) entropies demonstrate the possibility of constructing from shockwave data

TABLE 4

p , GPa	60	100	150	200
S , J/g·°K [17]	0,246	0,353	0,438	0,498
$T \cdot 10^{-3}$, °K	2,48	5,52	9,83	14,5
S , K/g·°K (4.1), (4.2)	0,266	0,365	0,447	0,509
$T \cdot 10^{-3}$, °K	2,78	5,90	9,88	13,75

thermodynamically complete ES of metals at pressures of hundreds of GPa, based on taking into account the thermal excitation of the electrons, fusion and certain simple assumptions concerning the heat capacity and Grüneisen ratio of the lattice. This conclusion and the experimental determination of the entropies on the Hugoniot adiabatics represent the principal result of our research.

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