

# Equations of State of Matter from Shock Wave Experiments

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An interpretation of the shock wave Hugoniot relation is made by using the Mie-Grüneisen equation of state. Isothermal pressure-volume curves for various metals are calculated from the data of McQueen and Marsh and Al'tshuler et al. A linear relation between shock wave velocity  $u_s$  and particle velocity  $u_p$  is assumed, and the numerical integration is extended beyond the range of the experiments. Independent calculations are made by using either the Slater or the Dugdale-MacDonald formula. Results thus obtained do not differ appreciably. The result for iron is in good agreement with that obtained by Al'tshuler et al., who used an experimentally determined value of the Grüneisen ratio. The equations of state thus calculated are well approximated by the Murnaghan-Birch equation of state with the second-order coefficient  $\xi$  varying from  $-\frac{1}{2}$  to  $\frac{1}{2}$ . The use of the TFD model is not valid below 100 Mb. However, inspection of the results gives the impression that for some metal the  $P$ - $\rho$  curve will approach the TFD curve at pressures higher than 100 Mb. The density and incompressibility of the earth's core are compared with those of iron. The general conclusion is that the density of the earth's core is about 1 to 1.5 g/cm<sup>3</sup> less than the density of iron at corresponding pressure and temperature. The difference in incompressibility is very small. Bullen's incompressibility-pressure hypothesis is tested on the basis of the result obtained here. The variation of the values of incompressibility among the metals studied here is too large even at the pressure of 4 Mb to support the hypothesis. A detailed inspection of the result for the incompressibility obtained here, however, implies that it is still difficult to avoid the conclusion arrived at from the incompressibility-pressure hypothesis that the inner core is solid.

## INTRODUCTION

Shock wave studies have provided valuable information for the study of the internal constitution of the earth. Rice et al. [1958] determined the equation of state for a number of materials to pressures of up to 500 kb. The agreement of their results with the static measurements of Bridgman could be regarded as a proof of the soundness of the basic assumptions. The pressure range was successively extended to 2 Mb by McQueen and Marsh [1960]. Al'tshuler et al. [1958a, b, 1960] studied the shock compression of various metals at still higher pressures (up to 4 to 5 Mb). As the shock wave experiments give the relationship between pressure  $P$  and volume  $v$  under the shock condition, it is necessary to introduce thermodynamical considerations in order to interpret them in terms of isothermal or adiabatic  $P$ - $v$  relations.

In the works of Rice et al. [1958] and McQueen and Marsh [1960] the Mie-Grüneisen equation of state and the Dugdale-MacDonald relation for the volume dependence of the Grüneisen ratio were introduced for the interpretation of the Hugoniot  $P$ - $v$  relation. On the other hand, Al'tshuler et al. performed an elaborate experiment using a reduced density sample to determine the Grüneisen ratio at high pressures. Using this and the Mie-Grüneisen equation of state, they determined the equation of state of iron. For other elements, however, equations of state were not given for lack of an experimentally determined Grüneisen ratio at high pressures.

In this paper we attempt to formulate as systematically as possible the method of interpreting the Hugoniot  $P$ - $v$  relation and then to make the Hugoniot data so far determined readily available for use in various geophysical problems. We also discuss the equation of state in relation to the Murnaghan-Birch equation of

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state for moderately high pressure and the Thomas-Fermi-Dirac equation of state for extremely high pressures. The variation with pressure of incompressibility  $k$ , Debye's temperature  $\Theta$ , and the Grüneisen ratio  $\gamma$  are also calculated. The method is also extended to the calculation of isothermal pressure-density relations for elevated temperatures. All these data are used in discussing problems of basic geophysical interest, such as Bullen's incompressibility-pressure hypothesis and the distribution of density and incompressibility in the earth's core.

#### METHOD OF INTERPRETATION

Shock wave experiments determine the shock wave velocity  $u_s$  and particle velocity  $u_p$  in the sample. Using the laws of conservation of mass, momentum, and energy, we can derive the following relations [Rice *et al.*, 1958]:

$$u_s = v_{H0}[(P_H - P_{H0})/(v_{H0} - v)]^{1/2} \quad (1)$$

$$u_p = [(P_H - P_{H0})(v_{H0} - v)]^{1/2} \quad (2)$$

$$E_H = E_{H0} + \frac{1}{2}(P_H - P_{H0})(v_{H0} - v) \quad (3)$$

where  $v$ ,  $P_H$ , and  $E_H$  denote the specific volume, pressure, and internal energy of the sample under shock compression.  $v_{H0}$ ,  $P_{H0}$ , and  $E_{H0}$  are the quantities corresponding to the state before the passage of the shock front. A set of  $u_s$  and  $u_p$  values determined experimentally under various shock pressures provides a Hugoniot  $P$ - $v$  relation through (1) and (2). Generally,  $u_s$  and  $u_p$  for a single material can conveniently be expressed by the relation

$$u_s = C_0 + \lambda u_p \quad (4)$$

where  $C_0$  and  $\lambda$  are constants characteristic of the material considered. Although this relation does not seem to have any theoretical basis, it fits the data remarkably well [Alder, 1963]. By introducing the relation, we can express the experimental results simply by the two parameters  $C_0$  and  $\lambda$ , which in turn give an explicit Hugoniot relation through (1), (2), and (4) as

$$P_H = P_{H0} + \frac{C_0^2(v_{H0} - v)}{[v_{H0} - \lambda(v_{H0} - v)]^2} \quad (5)$$

Since  $P_H$  denotes the pressure under the shock condition with elevated temperature, it is necessary to remove from it the temperature effect to obtain the 0°K isothermal equation of state.

For this purpose the Mie-Grüneisen equation of state is introduced:

$$P_H - P_K = \gamma(E_H - E_K)/v \quad (6)$$

where  $\gamma$  is Grüneisen's ratio and  $P_K$  is the pressure necessary for compressing at 0°K a material to a state having the same specific volume  $v$  as that under the shock compression.  $E_K$  is the internal energy for the 0°K isothermal compression and is related to  $P_K$  by

$$P_K = -(\partial E_K/\partial v)_T \quad (7)$$

Putting (3) into (6) leads to

$$\gamma = \frac{v(P_H - P_K)}{\frac{1}{2}(P_H - P_{H0})(v_{H0} - v) + E_{H0} - E_K} \quad (8)$$

The volume dependence of Grüneisen's ratio was given by Slater and later by Dugdale and MacDonald [see Rice *et al.*, 1958]. Both formulas can be written as

$$-2(\gamma + \beta)/v = \frac{d^2(P_K v^\alpha)}{dv^2} / \frac{d(P_K v^\alpha)}{dv} \quad (9)$$

where  $\alpha$  and  $\beta$  are constants. In Slater's formula  $\alpha = 0$  and  $\beta = 2/3$ , and in Dugdale and MacDonald's formula  $\alpha = 2/3$  and  $\beta = 1/3$ . Equations 7, 8, and 9 are the basic equations determining the 0°K isothermal  $P$ - $v$  relation of the material. In integrating these, we used the following procedures. We let  $v_{K0}$  be the specific volume of the material at 0°K and zero pressure. Introducing new variables  $x$  and  $q_K$ , defined by

$$x = v_{K0}/v - 1 \quad (10)$$

and

$$\partial P_K/\partial x = q_K \quad (11)$$

we can rewrite (7), (8), and (9) as

$$\partial E_K/\partial x = v_{K0}P_K/(1+x)^2 \quad (12)$$

$$\frac{\partial q_K}{\partial x} = \frac{2}{1+x} (\gamma - \frac{1}{3}) q_K \quad (\text{Slater}) \quad (13)$$

$$\frac{\partial q_K}{\partial x} = \frac{2\gamma}{1+x} q_K - \frac{4}{3} \frac{1}{(1+x)^2} \cdot (\gamma + \frac{1}{6}) P_K \quad (\text{Dugdale-MacDonald}) \quad (13a)$$

where

$$\gamma = (P_H - P_K) / \left\{ \frac{1}{2} P_H \left[ \frac{v_{H0}}{v_{K0}} (1+x) - 1 \right] + \frac{(1+x)}{v_{K0}} [E_{H0} - E_K] \right\} \quad (14)$$

Equations 11, 12, 13 (or 13a), and 14 form a set of differential equations to determine  $E_K$ ,  $P_K$ ,  $q_K$ , and  $\gamma$ . In these equations,  $P_H$  is experimentally determined as in (5) and can be explicitly written by using the new variable  $x$  as

$$P_H = \frac{C_0^2}{v_{H0}} (1 + x) \cdot \frac{x + (1 - v_{K0}/v_{H0})}{[x(1 - \lambda) + 1 - \lambda(1 - v_{K0}/v_{H0})]^2} \quad (15)$$

$E_{H0}$  is the internal energy in the normal state (20°C, 1 atm) and can be calculated by Debye's formula

$$E_{H0} = \frac{3KT N_0}{w} u\left(\frac{\Theta}{T}\right) \quad (16)$$

where  $K$ ,  $N_0$ ,  $w$ , and  $\Theta$  are Boltzmann's constant, Avogadro's number, atomic weight, and Debye's temperature, respectively. The function  $u$  is given by

$$u(x) = \frac{3}{x^3} \int_0^x \frac{\xi^3}{e^\xi - 1} d\xi \quad (17)$$

which is tabulated in a number of textbooks [see, e.g., *Knopoff*, 1963].

The value of  $v_{x0}$  is not known at first but can be estimated in the following manner. Because the difference between  $v_{H0}$  and  $v_{K0}$  is due to thermal expansion,  $v_{K0}$  can be written as

$$v_{K0} = v_{H0} \left( 1 - \int_0^{293} \alpha dT \right) \quad (18)$$

where  $\alpha$  is the thermal expansion coefficient. Introducing the thermodynamical relation

$$\alpha = \gamma C / k v \quad (19)$$

where  $C$  and  $k$  denote the specific heat at constant pressure and the adiabatic incompressibility, and making use of the fact that  $\gamma$ ,  $k$ , and  $v$  all vary slowly with temperature, we can write (18) as

$$v_{K0} \approx v_{H0} \left( 1 - \frac{\gamma_{H0}}{k_{H0} v_{H0}} \int_0^{293} C dT \right) \approx v_{H0} \left( 1 - \frac{\gamma_{H0} E_{H0}}{k_{H0} v_{H0}} \right) \quad (20)$$

In the last equation in (20), we neglect a small difference between the specific heat at constant pressure and constant volume. For all the ele-

ments except iron, we used the thermodynamically determined values of  $\gamma$  listed by *McQueen and Marsh* [1960]. For iron we used the relation

$$\gamma_{H0} = 2\lambda - 1 \quad (21)$$

The value thus obtained is 2.16, which is close to the experimentally determined value 1.95 given by *Al'tshuler et al.* [1958]. The values of  $k_{K0}$  are estimated for the foot of the Hugoniot curve, namely,

$$k_{H0} = -v_{H0} \left( \frac{\partial P_H}{\partial v} \right)_{v_{H0}} = \frac{C_0^2}{v_{H0}} \quad (22)$$

Given all these values  $v_{K0}$  can readily be estimated.

The initial conditions necessary for the integration of (11), (12), and (13) are

$$P_K = 0 \quad E_K = 0 \quad \text{at } x = 0 \quad (23)$$

$$q_K = C_0^2 / v_{H0}$$

The first and second conditions are evident, but the third condition which gives the initial slope of  $P_K$  might require explanation. Although there is no theoretical estimation of the initial slope of the  $P_K$  curve, the initial slope of the Hugoniot  $P_H$  probably approximates it closely, because at the foot of the Hugoniot the temperature is not greatly raised and we can neglect a small difference between the isothermal  $\partial P_K / \partial v$  and adiabatic  $\partial P_H / \partial v$  slope. The slope at the foot of the Hugoniot is, as shown in (22),  $C_0^2 / v_{H0}$ , which is now used as the initial value of  $q_K$ . We can avoid the estimation of  $v_{K0}$  as in (18) by starting our numerical integration from  $v = v_{H0}$ . In this case, however, we must estimate  $P_K$  and  $E_K$  at  $v = v_{H0}$ , which are not zero, and in estimating them we must use approximations such as are used in (18)–(20).

We numerically integrate for Fe, Cu, Zn, Ag, Cd, Au, and Pb using the data of *Al'tshuler et al.* [1958] and for Ag, Au, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sn (gray), Sn (white), Th, Ti, Tl, V, W, and Zn using the data of *McQueen and Marsh* [1960]. The integrations for each metal are made twice, first with the Slater formula and then with the Dugdale-MacDonald formula. All the constants in the calculations are summarized in Table 1.

In Table 2 to 4, part of the results obtained by using the data of *Al'tshuler et al.* are given.

TABLE 1. Summary of Constants Used in the Calculation

$Z$	$w$	$\gamma_{H_0}^*$	$C_0, \dagger$ km/sec	$\lambda \dagger$	$E_{H_0},$ $10^8$ ergs	$\nu_{H_0}, \dagger$ $\text{cm}^3/\text{g}$	$\Theta_0, \dagger$ $^\circ\text{K}$	
Ag	47	107.88	2.55	3.3	1.54	5.03	0.09533	225
Au	79	197.0	3.29	3.15	1.47	2.98	0.0518	165
Cd	48	112.41	2.32	2.65	1.48	4.35	0.116	300
Cu	29	63.54	2.00	3.9	1.46	6.24	0.112	445
Fe	26	55.85	2.16	3.8	1.58	6.88	0.127	467
Pb	82	207.21	2.77	2.3	1.27	3.12	0.0882	94.5
Zn	30	65.38	2.45	3.2	1.45	7.38	0.140	308
Ag	47	107.88	2.55	3.243	1.586	5.09	0.0953	215
Au	79	197.00	3.29	3.075	1.560	2.96	0.0520	170
Cd	48	112.41	2.32	2.443	1.671	5.56	0.1157	120
Co	27	58.94	1.97	4.748	1.330	7.34	0.1134	385
Cr	24	52.01	1.19	5.217	1.465	7.47	0.1408	460
Cu	29	63.54	2.00	3.958	1.497	7.52	0.1124	315
Mo	42	95.95	1.52	5.157	1.238	4.54	0.0980	380
Ni	28	58.71	1.83	4.646	1.445	7.48	0.1129	375
Pb	82	207.21	2.77	2.028	1.517	3.15	0.0882	88
Sn	50	118.70	2.11	2.640	1.476	4.35	0.1374	260
						4.92		170
Th	90	232.05	1.26	2.132	1.278	2.77	0.0856	100
Ti	22	47.90	1.09	4.779	1.089	9.08	0.2217	380
Tl	81	204.39	2.25	1.859	1.515	3.16	0.0845	96
V	23	50.95	1.29	5.108	1.210	8.43	0.1639	390
W	74	183.86	1.54	4.005	1.268	2.02	0.0522	310
Zn	30	65.38	2.45	3.050	1.559	8.19	0.1400	234

\* From *McQueen and Marsh* [1960].† For the top set, from *Al'tshuler et al.* [1958]; for the bottom set, from *McQueen and Marsh* [1960].‡ For the top set, from *Kittel* [1956]; for the bottom set, from *Launay* [1956].

TABLE 2. Summary of Calculation for Silver

$V_{K_0}$	Dugdale-MacDonald							Slater					
	$P_{H_0}$ Mb	$P_{K_0}$ Mb	$k,$ Mb	$\gamma$	$E_{K_0},$ $10^{10}$ ergs	$\Theta,$ $^\circ\text{K}$	$T_{H_0},$ $^\circ\text{K}$	$P_{K_0},$ Mb	$k,$ Mb	$\gamma$	$E_{K_0},$ $10^{10}$ ergs	$\Theta,$ $^\circ\text{K}$	$T_{H_0},$ $^\circ\text{K}$
1.00	0.01	0	1.14	2.57	0	225	300	0	1.14	2.57	0	225	300
1.10	0.16	0.15	1.96	2.00	0.06	283	430	0.14	1.91	2.31	0.06	287	440
1.20	0.38	0.35	2.81	1.54	0.23	327	740	0.35	2.79	1.80	0.22	341	780
1.30	0.69	0.62	3.82	1.66	0.52	372	1,600	0.61	3.81	1.76	0.51	393	1,600
1.40	1.13	0.94	5.12	1.70	0.91	422	3,300	0.94	5.06	1.75	0.90	448	3,500
1.50	1.73	1.35	6.69	1.67	1.42	474	6,400	1.34	6.58	1.71	1.41	505	6,600
1.60	2.59	1.84	8.54	1.62	2.04	527	12,000	1.81	8.35	1.66	2.02	563	12,000
1.70	3.80	2.42	10.67	1.57	2.78	580	22,000	2.38	10.39	1.60	2.74	621	21,000
1.80	5.54	3.10	13.09	1.53	3.62	634	35,000	3.04	12.08	1.56	3.57	680	36,000
1.90	8.07	3.88	15.80	1.49	4.58	688	57,000	3.79	15.25	1.51	4.51	739	62,000
2.00	11.88	4.76	18.81	1.45	5.64	742		4.65	18.08	1.47	5.55	797	
2.10	17.79	5.76	22.12	1.41	6.82	795		5.60	21.16	1.43	6.70	856	
2.20	27.43	6.87	25.72	1.38	8.10	849		6.66	24.50	1.39	7.94	914	
2.30	44.21	8.10	29.60	1.33	9.49	901		7.83	28.07	1.34	9.29	971	
2.40	76.31	9.44	33.75	1.29	10.98	953		9.10	31.86	1.30	10.73	1027	
2.50	147.3	10.91	38.15	1.25	12.58	1004		10.48	35.84	1.25	12.26	1082	
2.60	348.3	12.50	42.76	1.20	14.27	1053		11.97	39.97	1.20	13.89	1135	
2.70	1,320	14.20	47.55	1.15	16.06	1101		13.56	44.22	1.15	15.59	1186	
2.80	67,766	16.02	52.50	1.09	17.94	1147		15.24	48.56	1.09	17.39	1236	

TABLE 3. Summary of Calculation for Iron

$V_{K0}$ $V$	Dugdale-MacDonald							Slater					
	$P_H$ , Mb	$P_K$ , Mb	$k$ , Mb	$\gamma$	$E_K$ , $10^{10}$ ergs	$\Theta$ , $^{\circ}$ K	$T_H$ , $^{\circ}$ K	$P_K$ , Mb	$k$ , Mb	$\gamma$	$E_K$ , $10^{10}$ ergs	$\Theta$ , $^{\circ}$ K	$T_H$ , $^{\circ}$ K
1.00	0.01	0	1.14	2.18	0	467	290	0	1.14	2.18	0	467	290
1.10	0.16	0.14	1.90	2.20	0.07	580	400	0.14	1.86	2.51	0.07	587	400
1.20	0.38	0.35	2.86	1.80	0.30	688	670	0.34	2.84	2.04	0.29	717	690
1.30	0.70	0.62	3.98	1.74	0.68	792	1,300	0.61	3.96	1.83	0.67	835	1,300
1.40	1.16	0.96	5.37	1.73	1.22	900	2,600	0.95	5.31	1.78	1.20	954	2,700
1.50	1.81	1.39	7.06	1.71	1.92	1014	5,100	1.37	6.93	1.75	1.89	1077	5,100
1.60	2.75	1.91	9.06	1.67	2.77	1130	9,400	1.88	8.85	1.71	2.74	1205	10,000
1.70	4.11	2.52	11.40	1.63	3.79	1249	16,000	2.48	11.08	1.67	3.74	1334	17,000
1.80	6.14	3.25	14.07	1.59	4.97	1370	30,000	3.19	13.63	1.62	4.90	1466	29,000
1.90	9.23	4.09	17.10	1.56	6.31	1492	50,000	4.00	16.50	1.58	6.21	1598	50,000
2.00	14.10	5.05	20.49	1.52	7.82	1614	85,000	4.92	19.68	1.53	7.68	1731	87,000
2.10	22.18	6.14	24.23	1.48	9.49	1737	150,000	5.97	23.18	1.49	9.31	1863	140,000
2.20	36.58	7.36	28.32	1.43	11.32	1858		7.13	26.98	1.44	11.08	1995	
2.30	64.95	8.72	32.75	1.39	13.31	1978		8.42	31.06	1.39	13.01	2124	
2.40	130.5	10.21	37.49	1.34	15.46	2096		9.83	35.39	1.34	15.08	2251	
2.50	332.1	11.84	42.50	1.28	17.76	2212		11.37	39.93	1.28	17.30	2375	
2.60	1,535	13.61	47.76	1.22	20.22	2323		13.03	44.63	1.22	19.66	2495	
2.70	9,859	15.51	53.20	1.16	22.82	2430		14.80	49.45	1.16	22.14	2610	

Other results obtained will be given elsewhere. The  $P_K$ - $\rho$  ( $= 1/v$ ) relations for seven metals thus obtained are shown in Figures 1 to 7.

As is easily seen from (5),  $P_H$  becomes infinitely large when  $v$  reaches the value  $V_{H0}$   $(\lambda - 1)/\lambda$ . The physical significance of this is not clear [Alder, 1963], but the function cannot be integrated beyond this limit. As the value of  $\lambda$  is around 1.5 for most of the metals, this limit is set at  $v \approx 0.3v_{H0}$  or  $x \approx 2$ . In the present study, we assumed that the linear relation (4)

was valid at the high pressures not covered by the experiment, and we integrated up to  $v \approx v_{H0} (\lambda - 1)/\lambda$ , where the volume was about one-third of the initial value. It should be noted that this is just an extrapolation. The Hugoniot at 4 Mb, say, is almost certainly in the melting range, which means that different  $C_0$  and  $\lambda$  should be used.

#### VARIATION OF $\gamma$ , $\Theta$ , AND TEMPERATURE

The Grüneisen ratio  $\gamma$  has been determined as a function of volume by using (14). The variation with volume of the Debye temperature  $\Theta$  can also be determined by integrating the basic formula [see Knopoff, 1963].

$$\gamma = -(v/\Theta)(d\Theta/dv) \quad (24)$$

Tables 2 and 3 include the variation of  $\gamma$  and  $\Theta$  thus obtained.

Having determined the values of  $P_K$ ,  $\gamma$ , and  $\Theta$  as functions of volume, we can calculate the temperature along the Hugoniot as well as the thermal pressure, pressure necessary to offset the effect of thermal expansion, from which in turn, if necessary, isotherms at arbitrary temperatures can be obtained. The procedure is as follows. Combining the Mie-Grüneisen equation of state with Debye's formula for the thermal

TABLE 4. Comparison of the Result for Iron with the Result Obtained by Al'tshuler et al. [1958]

$V_0$ $V$	Al'tshuler et al. [1958]	$P_K$ , Mb Dugdale-MacDonald	Slater
1.25	0.463	0.47	0.47
1.30	0.600	0.62	0.61
1.35	0.761	0.78	0.77
1.40	0.942	0.96	0.95
1.45	1.154	1.17	1.15
1.50	1.358	1.39	1.37
1.55	1.613	1.64	1.62
1.60	1.880	1.91	1.88
1.65	2.174	2.20	2.17
1.70	2.484	2.52	2.48
1.75	2.822	2.87	2.82

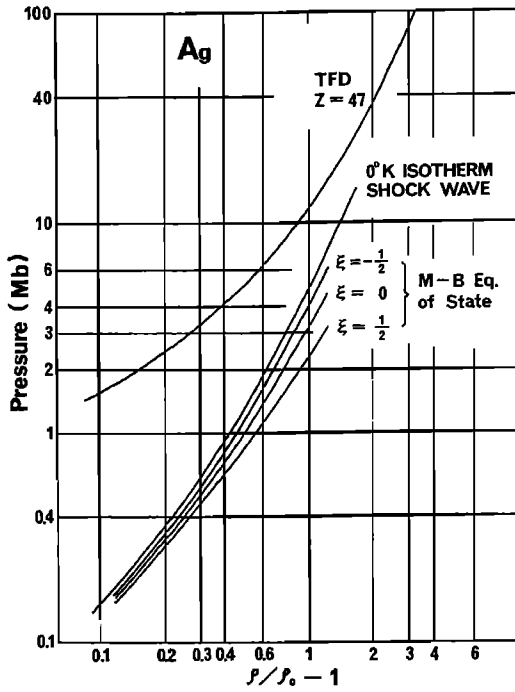


Fig. 1. Isotherms of silver at 0°K based on shock wave data, Murnaghan-Birch model and Thomas-Fermi-Dirac model.

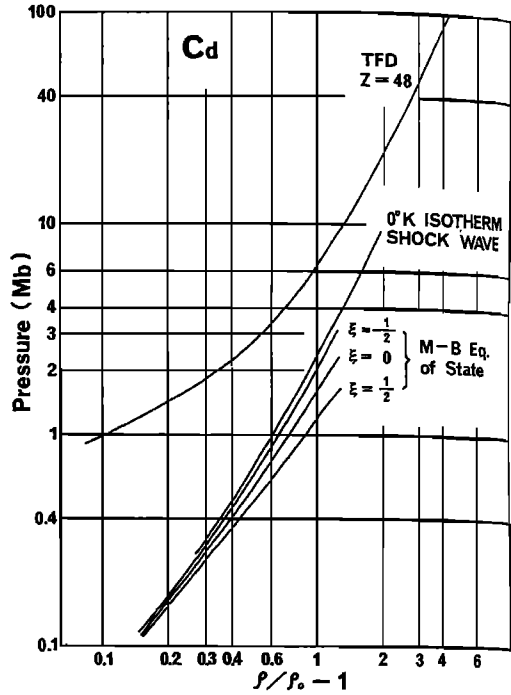


Fig. 3. Isotherms of cadmium at 0°K.

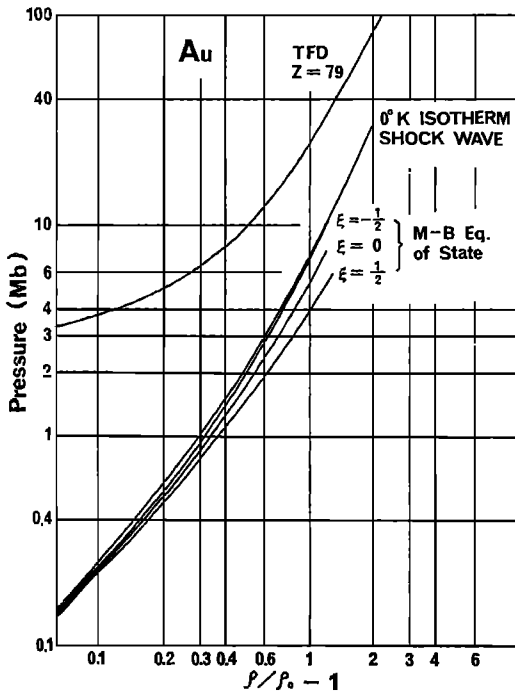


Fig. 2. Isotherms of gold at 0°K.

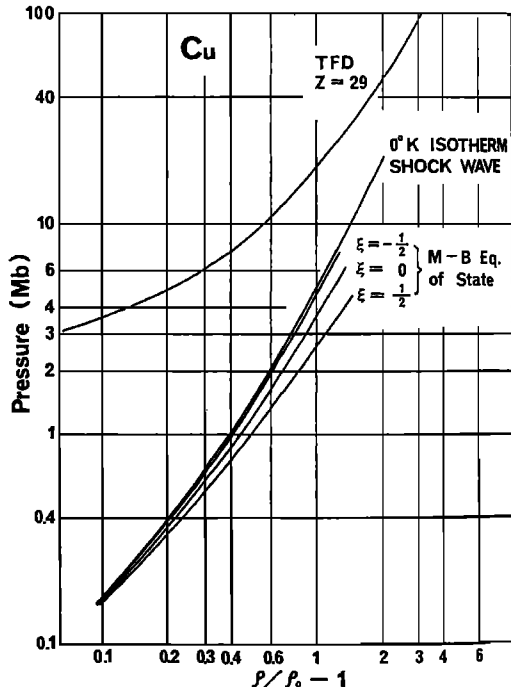


Fig. 4. Isotherms of copper at 0°K.

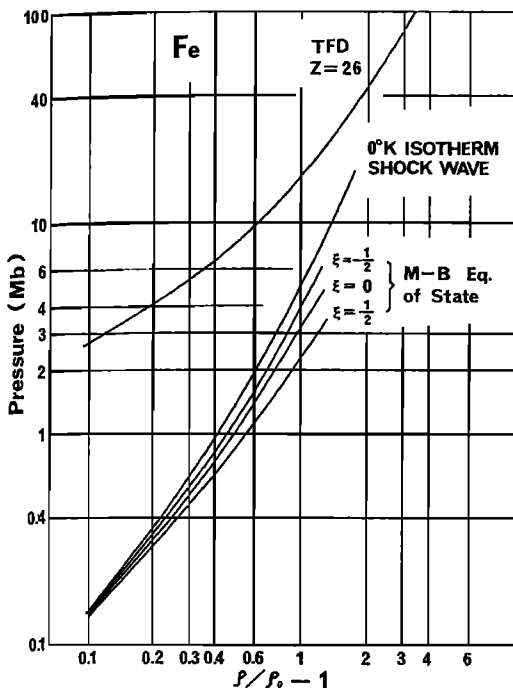


Fig. 5. Isotherms of iron at 0°K.

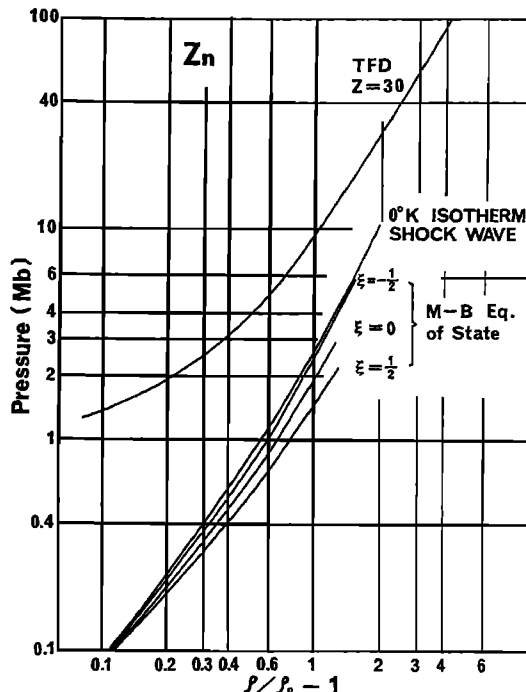


Fig. 7. Isotherms of zinc at 0°K.

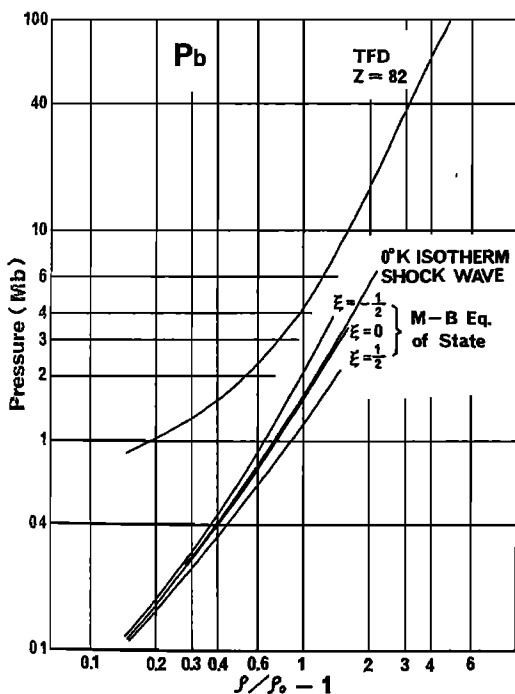


Fig. 6. Isotherms of lead at 0°K.

energy, we obtain

$$P - P_K = (\gamma/v)3N_0K(T/w)u(\Theta/T) \quad (25)$$

where  $P$  is the pressure necessary to compress a material to the state having specific volume at temperature  $T$ . Since  $P_K$ ,  $\gamma$ , and  $\Theta$  are all known as functions of  $v$ , the isotherm at temperature  $T$  can be calculated by adding the right-hand side of (25) to  $P_K$ . Similarly,  $T$  along the Hugoniot can be determined by equating  $P_H$  to  $P$  in (25) and solving it for  $T$ . The values of  $T$  thus determined are given in Tables 2, 3, and 4.

#### DISCUSSION OF THE RESULTS

In Table 4, the result obtained here for iron is compared with that obtained by *Al'tshuler et al.* [1958] in which the Grüneisen ratio is experimentally determined. The agreement of the present result with that of *Al'tshuler et al.* is remarkable. No such comparison can be made for other metals because of lack of experimentally determined values of Grüneisen's ratio at high pressures. However, the close agreement found for iron implies the appropriateness of the present method for the interpretation of the

Hugoniot relations for other metals. Also, the difference between the results based on the Dugdale-MacDonald formula and the Slater formula is negligible. For Ag, Au, Cd, Cu, Pb, and Zn, the calculation was based on the data of both Al'tshuler et al. and McQueen and Marsh. Although the discrepancy between the results from the two sets of data is small for Ag, Au, Cu, and Zn, appreciable differences were observed for Cd and Pb. This result is not unexpected because the values of  $C_0$  and  $\lambda$ , which mainly determine the equation of state, differ considerably (Table 1). For the above six,  $P$ - $v$  curves in Figures 1 to 7 are from the data of Al'tshuler et al.

The equations of state at 0°K calculated here are compared with the Murnaghan-Birch and Thomas-Fermi-Dirac equations of state. The Murnaghan-Birch equations of state are calculated for  $\xi = -\frac{1}{2}, 0, \frac{1}{2}$ . The Thomas-Fermi-Dirac equations represented here are based on the calculations of *Metropolis and Reitz* [1951], who determined the potential function  $\psi$  as a function of nondimensional radius  $x$  and gave the value  $\psi(x_0)$  at the outer boundary of atoms  $x_0$ . Using these values, we get pressure  $P$  and density  $\rho$  of an element with atomic number  $Z$ :

$$P = \frac{Z^2 e^2}{10\pi\mu^4} \left[ \left( \frac{\psi(x_0)}{x_0} \right)^{1/2} + \epsilon \right]^5 \cdot \left[ 1 - \frac{5\epsilon/\psi}{(\psi(x_0)/x_0)^{1/2} + \epsilon} \right] \quad (26)$$

$$\rho = 3Z M_p / 2\pi(\mu x_0)^3$$

where  $e$  and  $M_p$  are the electron charge and mass of proton, respectively, and  $\mu$  and  $G$  are constants given by

$$\mu = 0.46848Z^{-1/3} \quad (27)$$

$$G = 0.21178Z^{-2/3}$$

$P$ - $\rho$  curves thus calculated for elements of atomic numbers  $Z = 14, 29, 33, 49, 61,$  and  $92$  are given in Figure 8. The  $P$ - $\rho$  relations for the metals studied here are obtained by graphical interpolation.

Comparison of the 0°K isotherm obtained here for various metals with  $P$ - $\rho$  relations based on the Murnaghan-Birch and Thomas-Fermi-Dirac models are shown in Figures 1 to 7. It can be seen that at lower pressures the Murnaghan-Birch

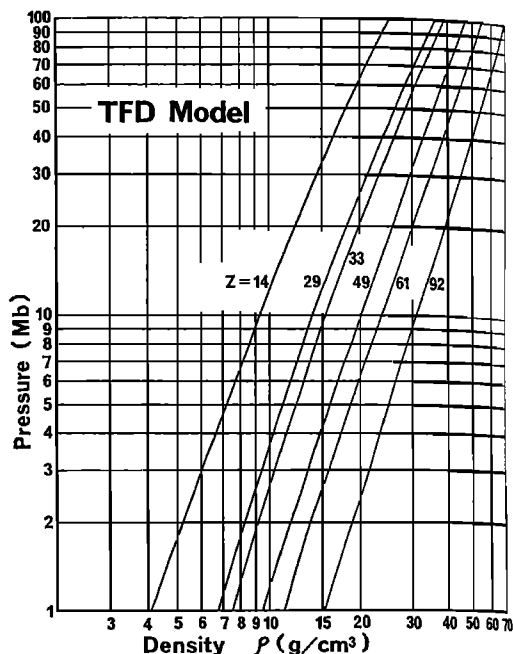


Fig. 8. Pressure-density relationships for the Thomas-Fermi-Dirac model of elements at 0°K.

curves with  $\xi = 0 \approx -\frac{1}{2}$  fit the  $P$ - $\rho$  relations of all the metals except titanium, for which the  $P$ - $\rho$  curve is approximated by a Murnaghan-Birch curve with  $\xi = \frac{1}{2}$ . In other words, although the Murnaghan-Birch equation of state with  $\xi = 0$  does not approximate the equations of state of all the metals studied here as it does for a number of alkali metals [Birch, 1952], the equation of state having a small second-order coefficient  $\xi$  is quite appropriate for most of them. This second-order coefficient  $\xi$  may vary from one metal to another, and it can be said that the equation of state of metals can essentially be determined by the two material constants,  $k_{H0}$  and  $\xi$ . For some metals, such as Ag, Cr, and Fe, it can be seen that the 0°K isotherm would deviate from the Murnaghan-Birch curve and merge into the Thomas-Fermi-Dirac curve at pressures a little higher than 100 Mb.

In Figure 9, we compare calculated density and incompressibility of iron with those of the earth's core. Three density curves are calculated for temperatures 0°K, 3000°K, and 6000°K by the method explained above. The temperature effect becomes small with increasing pressure. This figure shows that the density of the



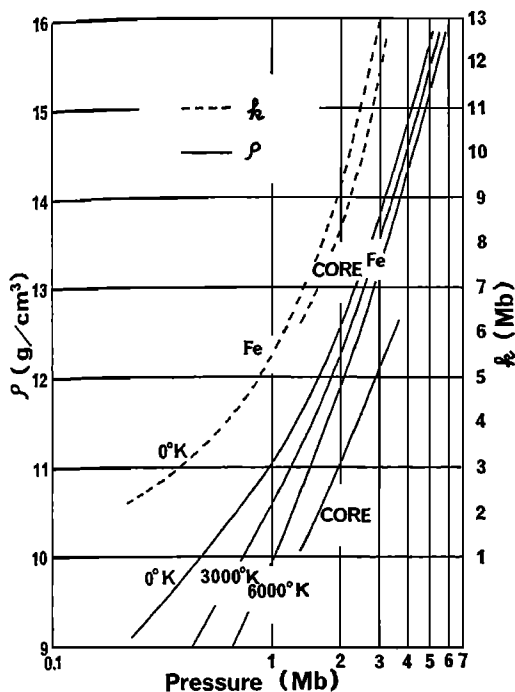


Fig. 9. Comparison of density and incompressibility curves for iron with those for the earth's core. Density distribution is based on Birch's solution I.

earth's core is 1 to 1.5 g/cm<sup>3</sup> smaller than that of iron at the pressure and temperature prevailing in the earth's core. The incompressibility curve of iron at 0°K is almost parallel to, and about 1 Mb larger than, the incompressibility curve of the core. These results support the view [Knopoff and MacDonald, 1960] that the earth's core is composed of iron, silicon, and carbon.

The incompressibility-pressure hypothesis advanced by Bullen [1949] can be tested on the basis of the results obtained here. This hypothesis says that above a certain pressure the incompressibility  $k$  is independent of the chemical composition and depends only on the pressure. In Table 5 are listed the values of the incompressibility of the metals at 0°K and at pressures of 0, 1, and 4 Mb. The range of the variation of the values of incompressibility among the metals studied here can be expressed by

$$R = 2(k_{\max} - k_{\min}) / (k_{\max} + k_{\min}) \quad (28)$$

where  $k_{\max}$  and  $k_{\min}$  are the maximum and

TABLE 5. Incompressibilities of Metals (in Mb)

Metal	$P_K$ , Mb		
	0	1	4
<i>Al'tshuler et al. [1958]</i>			
Ag	1.14	5.35	16.2
Au	1.92	6.69	16.8
Cd	0.61	4.36	13.9
Cu	1.36	5.35	15.5
Fe	1.14	5.52	16.8
Pb	0.60	3.65	10.9
Zn	0.73	4.44	13.8
<i>McQueen and Marsh [1960]</i>			
Ag	1.10	5.47	16.8
Au	1.82	6.13	17.9
Cd	0.52	5.00	16.3
Co	1.99	5.65	14.8
Cr	1.93	6.14	16.6
Cu	1.39	5.60	16.1
Mo	2.71	6.14	14.6
Ni	1.91	5.98	16.3
Pb	0.47	4.29	13.9
Sn (gray)	0.51	4.21	13.4
Sn (white)	0.51	4.23	13.4
Th	0.53	3.55	10.7
Ti	1.03	3.62	9.51
Tl	0.41	4.21	13.7
V	1.59	4.77	12.4
W	3.07	6.64	15.6
Zn	0.66	4.76	15.2
$R = \frac{2(k_{\max} - k_{\min})}{k_{\max} + k_{\min}}$	1.53	0.61	0.61

minimum values of the incompressibility.  $R$  decreases very rapidly from 1.53 to 0.61 when the pressure increases from 0 to 1 Mb. However,  $R$  does not change appreciably at pressures higher than 1 Mb. Consequently, it is expected that the incompressibility might differ from one material to another by at least 60% even at 4 Mb, which is approximately the pressure at the earth's center. The incompressibility-pressure hypothesis might not be true in a strict sense, but the important conclusion derived from this hypothesis, namely that a solid inner core accounts for the 10% increase in compressional wave velocity at the inner core boundary, might still be valid for the following reason. If the inner core is not solid, its incompressibility should be about 20% larger than that of the outer core. Since the incompressibility of the outer core is, as mentioned earlier, close to the incompressibility of iron, the incompressibility of the inner core should be about 20% larger than that of

iron. As shown in Table 5, it is rather difficult to find a metal that satisfies this requirement, and this could make it impossible for the inner core to be liquid.

### CONCLUSION

The Mie-Grüneisen equation of state combined with the Slater or the Dugdale-MacDonald formula for the Grüneisen ratio can successfully be used for the interpretation of Hugoniot  $P$ - $v$  relation in terms of the equation of state.

The result for iron obtained by this method is in good agreement with the result given by Al'tshuler et al. in which the value of Grüneisen's ratio at high pressure is experimentally determined. The use of either the Slater or the Dugdale-MacDonald formula does not make an appreciable difference in the final result. A comparison of the results with those obtained with the Murnaghan-Birch equation shows that the equation of state up to 10 Mb for the metals studied here can essentially be determined by two constants which are characteristic of each material. The first constant is the incompressibility which varies from one material to another. The second constant  $\xi$  takes a value between  $-1/2$  and  $1/2$  for many metals.

The TFD model gives densities that are too low even at 10 Mb, but an indication can be found in some metals that the  $P$ - $\rho$  curve will be well approximated by the TFD model at pressures slightly higher than 100 Mb.

The density of the earth's core is definitely less than that of iron at  $T = 3000^\circ\text{K}$ , and even at  $6000^\circ\text{K}$ .

The value of incompressibility at  $0^\circ\text{K}$  varies as much as 60% from one material to another, even at the pressure of 4 Mb. This does not support the incompressibility-pressure hypothesis, but a detailed inspection of the values of incompressibility at 4 Mb might rule out the possibility that the inner core is liquid.

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