Geophys. J. R. astr. Soc. (1972) **29**, 373–387.

The Melting Relations of Iron, and Temperatures in the Earth's Core

Francis Birch

(Received 1972 June 21)*

Summary

Thermodynamic data on the phases of iron are assembled in the form of speculative projections on the temperature–volume plane. Following a proposal by Kraut and Kennedy, the melting curves, for each phase, are assumed to be straight lines in this representation. As the position of the triple point, gamma-epsilon-liquid, is unknown, two hypothetical locations are considered: (1) at about 4 Mb, (2) at about 1 Mb. In the former case, the gamma phase is in equilibrium with the liquid at core pressures, in the latter, the epsilon phase. Nothing is known directly about the slopes of these melting curves, but the gamma melting temperatures are estimated to lie some 700° above the projection given by Higgins and Kennedy, with epsilon melting temperatures still higher. The relation of the isentropes of the liquid to these melting curves is also unknown, but 'conventional' isentropes, originating on the melting curve, may be found which lie in the liquid field at the pressures of the outer core.

Application to the Earth is complicated by the requirement for a light alloying element in the outer core; if the alloying element is silicon, a proportion of about 15 per cent by weight accounts satisfactorily for the density–velocity relation. The phase relations may be considerably modified by the presence of so much silicon: it is conjectured that the gamma phase is suppressed or confined to low pressures, that the epsilon phase will be the stable solid phase at core pressures, and that the isentrope originating at the melting temperature of the inner core-outer core boundary lies entirely in the liquid phase.

Introduction

The discovery of the inner core (Lehmann 1936) has led to repeated efforts to extract information about internal constitution and temperature from its seismic properties. The pressure at the boundary between inner core and outer core is approximately 3·4 Mb (megabars); the velocity V_P in the inner core is about $11{\cdot}2\,\mathrm{km\,s^{-1}}$, some 10 per cent higher than in the adjacent outer core. An interpretation which has found favour for a variety of reasons is that the inner core is the solid phase corresponding to the liquid outer core (Birch 1940; 1952; Bullen 1946, 1949, 1950 and many later papers; Ramsey 1950). Recent analyses of the periods of free oscillations, especially of the radial overtones, strongly support this idea, with relatively 'normal' values of rigidity and shear velocity required in the inner core.

*Received in original form 1972 May 16.

(Pekeris, Alterman & Jarosch 1962; Alsop 1963; Derr 1969; Jordan & Franklin 1971; Dziewonski & Gilbert 1917, 1972; Dziewonski 1971; see also Julian, Davies & Sheppard 1972 for possible observation of *PKJKP*). It may thus be postulated that the temperature at the boundary, at a depth of some 5150 km, lies on the freezing curve of core material. Though argument continues concerning the amount and nature of alloying elements, there remains little ground for doubting that both inner and outer cores consist mainly of iron. Higgins & Kennedy (1971; also Kraut & Kennedy 1966; Strong 1959) have used measurements of the melting temperature of iron under pressure as the basis of an estimate of core temperatures, finding 4250 °C for the melting point of iron at the pressure of the boundary between inner and outer cores. This is within the wide range of earlier estimates, but they also believe that the rise of melting temperature through the outer core is smaller than on an adiabatic curve originating at the boundary. This produces difficulties for convection in the liquid outer core, and already a number of suggestions for circumventing this supposed impediment to free circulation have appeared (Bullard & Gubbins 1971; Busse 1972; Malkus 1972). In view of the importance of core conditions for theories of the Earth's magnetic field, it seems worth while to examine these questions more fully.

We may distinguish several relatively independent questions: (1) What can be said about the melting relations of pure iron? (2) What is the relation of isentropes of liquid iron to the melting curve? (3) To what extent can we rely on the answers to these questions for conclusions about the Earth's core? A high degree of uncertainty surrounds all of these matters.

The extrapolation of the melting curve by Higgins & Kennedy rests on the observation (Kraut & Kennedy 1966) that a linear relation between melting temperature and volume, as measured at ordinary temperature, holds for a number of metals. Though most melting curves have been followed to compressions of only a few per cent, those of potassium and rubidium have been measured to compressions of nearly 50 per cent, of the same order as those in the core. Whether these straight lines are tangents to curves, such as are found for various compounds, need not be debated for the moment; as a first approximation, the Kraut–Kennedy law is supported by an impressive amount of evidence.

Melting of iron under pressure has been observed by several investigators (Strong 1959, 1961; Bundy & Strong 1962; Boyd & England 1963; Sterrett, Klement & Kennedy 1965), the highest nominal pressure reaching 96,000 atmospheres (Strong 1959; corrected (1961) to 60 000). These measurements are fairly consistent with linear dependence of melting temperature on either pressure or volume, the total compression reaching only a few per cent, and the experimental points showing deviations of the order of 10° from smooth curves. It was remarked by Sterrett *et al.* that their zero-pressure melting temperature (1513 °C) was notably lower than the value (1535 °C) for pure iron; the difference was attributed to impurities in the iron, contamination by oxygen and errors in temperature measurement. These authors conclude: 'Thus, anyone who extrapolates the present data from 0·040 to 3·2 Mb and deduces anything about the nature of the cores of the Earth does so very much at his own risk. The temperature uncertainties in any such extrapolation could conceivably be as great as ± 5000 °C.'

A more sanguine view was taken by Kraut and Kennedy, after remarking the linear relation between melting temperature and volume. The measurements by Sterrett *et al.* were put in the form, $T_m(°\mathrm{C}) = 1513\,(1+3{\cdot}3209\,\Delta V/Vo)$, where the compression, $\Delta V/Vo = (Vo-V)/Vo$, was taken from Bridgman's isothermal compressions for iron at ordinary temperature. With these numbers, and volumes at high pressures from Al'tshuler *et al.* (1958), extrapolation to 3 Mb gave 3724 °C.

Higgins and Kennedy revised the measurements of Sterett *et al.*, introducing a correction for the effect of pressure on the thermocouples (Getting & Kennedy 1970) which increased the rise of melting temperature for 40 kb (kilobars) from 117° to 140°. Combining this with the isothermal compression of 0·0233, they find the melting temperatures of iron at pressures equal to those in the Earth at depths of 2900 and 5100 km to be 3750 °C and 4250 °C, respectively. The extrapolation depends on the ratio of temperature rise, 140°, to volume compression, which in turn depends upon pressure and temperature calibrations in two different solid-medium systems; the correction for the pressure effect on the thermocouples, which is non-linear, is itself extrapolated nearly 700°. It is consequently difficult to assess the absolute accuracy of the temperature-volume ratio on which these extrapolations depend; but the initial slope determined by these experiments is in any case not the slope which is required for high pressures.

Discussions of the melting of iron have been remarkable in their neglect of the fact that iron exists in several crystalline forms, and that the melting curve defines a condition of equilibrium between the liquid phase and one of the solid phases. (See, however, Sterrett *et al.* 1965). Ignorance regarding the liquid state no doubt explains this in part; thus Lindemann's law is formulated in terms of properties of the solid alone, and most attempts to give a physical interpretation to Simon's empirical melting law are based on equations for solids.

Application of these theories to iron runs afoul of the circumstance that, beyond a relatively low pressure, the solid phase in equilibrium with the melt is not the phase (alpha) for which we know the initial melting point rise. Two denser phases, gamma and epsilon, are of primary interest for the geophysical problem, but knowledge of their thermodynamic properties is fragmentary. A review of this knowledge is undertaken below: the conclusions are inevitably speculative.

Phase diagram of iron

Four crystalline phases of iron are known: alpha, body-centred cubic; gamma face-centred cubic; delta, like alpha; epsilon, hexagonal close-packed. The thermodynamic parameters at the various transitions are given in Table 1, and tentative phase diagrams in Figs 1 and 2. The triple point, alpha-gamma-epsilon, is at about 110 kb and 750 kb (Johnson, Stein & Davies 1962; Takahashi & Bassett 1964, 1965; Bundy 1965; Giles, Logenbach & Marder 1971). The position of the gamma-epsilon-liquid triple point is largely conjectural, and two alternatives are considered. The slope of the gamma-delta phase line is taken as 6·2°/kb, and of the delta-liquid line, 3·3°/kb; the triple point delta-gamma-liquid is then at about 1970 K and 50 kb. It seems probable that all the measurements of melting refer to the melting of delta

Table 1

Volume and entropy changes at transitions, and slopes of phase boundaries

Transition	Pressure kb	Temperature °K	Δ V $cm^3\,mol^{-1}$	Δ S $J\,K^{-1}\,mol^{-1}$	dT/dP °/kb
alpha-gamma	0	1184	−0·075	0·79	−9·5
	110	750			−2·3
gamma-delta	0	1665	0·040	0·65	+6·2
delta-liquid	0	1808	0·28	8·4	$+3{\cdot}3_3$
gamma-liquid	0	1970	0·42	9·6	+4·4
	50	1970	0·36	9·3	+4·0
gamma-epsilon	~110	~750			+2(±1)
alpha-epsilon	~130	~300	−0·38		−30?

Sources of data: Hultgren *et al.* 1963; Johnson *et al.* 1962; Kirshenbaum & Cahill, 1962; Takahashi & Bassett 1964; Bundy 1965; Mao *et al.* 1967; Pearson 1967.

iron, and at most, serve to confirm, with relatively large uncertainties, the slope calculated from the thermodynamic quantities. This is not without value. In earlier work, the slope of the delta-gamma boundary was calculated to be nearly 14°/kb; this followed from a value of ΔS of 0·07 cal K^{-1} mol^{-1} as given in Kelley (1949). The more recent compilation by Hultgren *et al.* (1963) gives 0·156 cal K^{-1} mol^{-1}, or 0·65 JK^{-1} mol^{-1}, as shown in Table 1. There appears to be no experimental confirmation of the effect of pressure on this transition. Above 50 kb, the solid phase in equilibrium with the liquid is first the gamma phase and ultimately the epsilon phase, for neither of which are there any useful observations of melting.

The densities of the alpha, gamma, delta and liquid phases are known as functions of temperature at 1 atmosphere, and the density of the alphas and epsilon phases at the transition pressure of about 110 kb. Beyond about 130 kb, where alpha iron transforms to the epsilon phase, the volumes and pressures on the Hugoniot curve refer to the epsilon phase, until it melts or transforms to the gamma phase. The discontinuity at 130 kb in the shock compressions led to the discovery of the epsilon phase by Bancroft, Peterson & Minshall (1956; Johnson *et al.* 1962; Jamieson & Lawson 1962). The slope of the gamma-liquid boundary must be greater than 3·3°/kb and less than 6·2°kb, if we suppose that these slopes are insignificantly different at 50 kb from their initial values, a supposition roughly supported by the linearity

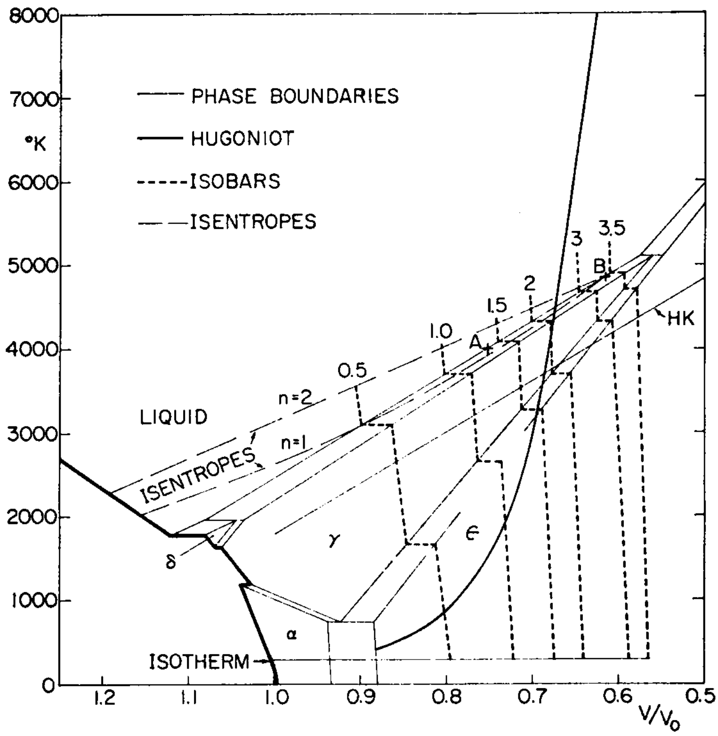

FIG. 1. Hypothetical projection of phase relations of iron on the temperature-volume plane, with the gamma-epsilon-liquid triple point at about 4 Mb, 5100°K. Hugoniot and isotherm from McQueen *et al.* (1970); pressures on isobars in megabars. The line 'HK' is the melting curve of Higgins and Kennedy. The crosses at 'A' and 'B' correspond to melting points at 1·3 and 3·4 Mb, respectively. Two conventional isentropes are shown, originating at 'B'; with the index, $n = 2$, the isentrope lies in the liquid field; with $n = 1$, the isentrope lies in the two-phase region in part, and is not correctly represented by the smooth curve.

of the melting temperatures versus pressure. If volume differences and entropy differences are applied without correction, the slope of the gamma-liquid boundary is 4·4°/kb; with somewhat uncertain corrections for the volume and entropy changes with pressure, this becomes 4·0°/kb.

We now wish to transfer the information from the $T-P$ plane to the $T-V$ plane. For any change of T and P for a given phase, $dV = V\alpha dT - VdP/K_T$, where V, specific volume, α thermal expansion, and K_T, isothermal incompressibility, all refer to the phase in question. Thus along the melting curve, characterized by a given $(dT/dP)_m$,

$$-V_0\left(\frac{dT}{dV}\right)_m = \frac{V_0 K_T(dT/dP)_m}{V[1-\alpha K_T(dT/dP)_m]}$$

Following Kraut & Kennedy (1966), we suppose this slope is constant. V_0 is the specific volume at $P = 0$, $T = 293$ K, and is introduced for convenience of reference to large compressions.

The numerical evaluation of this slope in the $T-V$ plane is subject to much uncertainty, whether for the gamma phase or the liquid; the only measurements of compressibility of iron are for the alpha phase, and extend only to 500 °C (Leese & Lord 1968). As a rough estimate for gamma iron at 1970 °K, let us take $K_T = 900$ kb, $\alpha = 70{\cdot}10^{-6}\ \mathrm{K}^{-1}$, $dK/dP = 6$, and suppose αK_T independent of pressure. With a

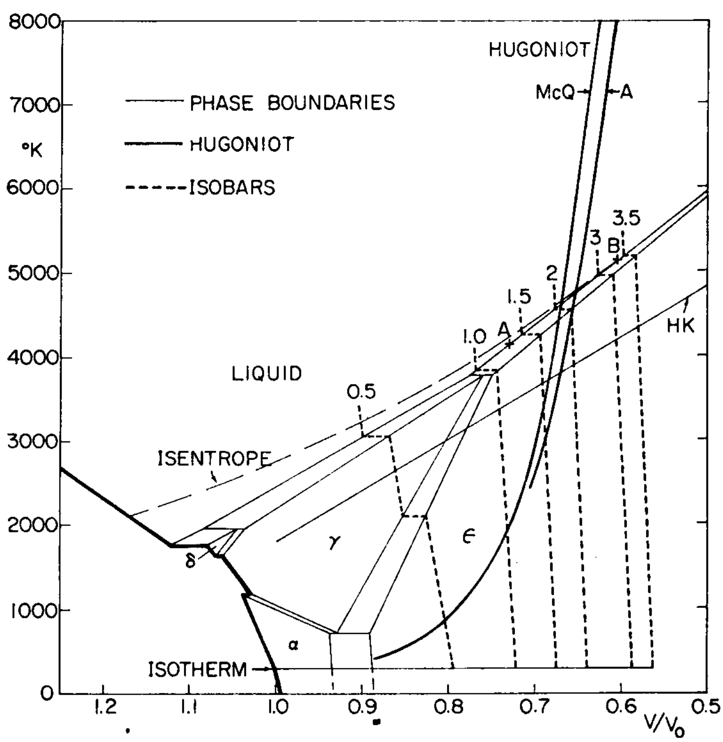

FIG. 2. Hypothetical projection of phase relations of iron on the temperature-volume plane, with the gamma-epsilon-liquid triple point at about 1 Mb, 3800°K. Hugoniot (McQ) and isotherm from McQueen *et al.* (1970); Hugoniot (A) from Al'tshuler *et al.* (1962); pressures on isobars in megabars. The line ' HK ' is the melting curve of Higgins and Kennedy. Points 'A' and ' B ' as in Fig. 1. The isentrope originating at ' B ', with $n = 1$, lies in the liquid field.

mean value for $(dT/dP)_m$ of 4·2°/kb, we obtain, for the gamma phase,

$$-V_0\left(\frac{dT}{dV}\right)_m = 6560\,°\mathrm{K} \qquad (1)$$

The evaluation for the liquid is still more hazardous, but the slope must be slightly less than for the solid, on the assumption that the volumes of the two phases become more nearly equal as pressure increases.

This slope is not greatly different from that proposed by Higgins and Kennedy, based on the compression and melting point rise of the alpha phase; their equation implies

$$-V_0\left(\frac{dT}{dV}\right)_m = 6009\,°\mathrm{K}. \qquad (2)$$

Their line originates at $V/V_0 = 1$, $T = 1808\,°\mathrm{K}$, whereas the line for the gamma phase originates at $V/V_0 = 1{\cdot}035$, $T = 1970\,°\mathrm{K}$; thus the temperatures implied by (1), on the assumption that $(dT/dV)_m$ is constant, are about 700° higher than those of Higgins & Kennedy. With the uncertainties of the calculation, even the initial slopes may be considerably in error, and possible curvature of the phase boundaries leaves a large area for disagreement.

Perhaps the most uncertain factor is the role of the epsilon phase. The initial slope, (dT/dP) of the gamma-epsilon boundary is given by Bundy as 2·8°/kb, by Takahashi & Bassett as 2 ± 1°/kb. There is some basis for supposing that in the $T-V$ plane, this boundary might curve upward, to intersect the gamma melting curve at some pressure lower than 1 Mb, but the phase boundaries have been represented as straight lines in Figs 1 and 2. In Fig. 1 the triple point gamma-epsilon-liquid is taken as 5100 °K, $\sim$4 Mb; in Fig. 2, the triple point is at 3800 °K, $\sim$1 Mb. These choices are significant with respect to core pressures and to the estimated temperatures on the Hugoniot curve of iron. In Fig. 1, the gamma phase is the solid phase at the melting point throughout the range of pressure in the Earth's core, and the Hugoniot curve passes through the gamma field before entering the liquid field. In Fig. 2, the epsilon phase is the solid phase at core pressures, the and Hugoniot remains in the epsilon filed until it reaches the liquid field. The epsilon phase is some 6 per cent denser than the alpha phase, or 4 per cent denser than the gamma phase, at low pressure, and the slope $(dT/dP)_m$ for the epsilon phase must be steeper than that of the gamma phase at the triple point. Again the representation in the $T-V$ plane is largely conjectural; in Fig. 2, the epsilon phase boundaries have been drawn as straight lines, with steeper slopes than those of the gamma boundaries. The temperatures of melting at core pressures are consequently higher than those projected for the gamma phase.

Figs 1 and 2 show the $T-V$ curve for the Hugoniot as given by McQueen *et al.* (1970), together with isobars, drawn to connect the pressures on the isotherm with the corresponding points on the temperature curve. Where an isobar intersects a phase boundary, it must change course in the $T-V$ diagram, continuing at constant temperature from the boundary of one phase to the boundary of the phase in equilibrium, where it again resumes a rise dependent upon the thermal expansion. In Fig. 1, isobars for pressures beyond the alpha-gamma-epsilon triple point are refracted twice in this way, on passage from epsilon to gamma, and again on passage from gamma to liquid. In Fig. 2, the isobars are refracted only once, at the passage from epsilon to liquid. No serious reliance can be placed on the exact co-ordinates of these lines, but in principle, they come closer to the physical reality than a single line in the $T-V$ plane.

One might hope that arguments based on the shock-wave experiments could lead to a choice between these two alternatives (or the third possibility, that the triple point lies somewhere within the range of core pressures), but there seems to be no clear evidence either way. Though melting is inferred behind strong shocks for a number of metals (McQueen & Marsh 1960) the basic observations of shock velocity versus particle velocity show no anomalies at the supposed melting points. Measurements on iron extend to very high pressures, but there are relatively few observations beyond 2 Mb, and in view of the experimental scatter small offsets would be difficult to find. It would be of great interest to determine whether the point on the Hugoniot at 1·6 Mb, for example, corresponds to the epsilon, gamma, or even the liquid, phase, as such a determination would discriminate among several conceivable disposition of phase lines.

Table 2

Temperatures and compressions on the Hugoniot curve of iron

Pressure Mb	Temperature °K			V/Vo	
	McQueen & Marsh 1960	McQueen *et al.* 1970	Al'tshuler *et al.* 1962	McQueen 1970	Al'tshuler *et al.* 1962
0	293	293	293	1·0000	1·0000
0·5	800	820		0·8005	
1·0	1750	1953	2050	0·7317	0·7386
1·5	2650	3473		0·6896	
2·0		5264	4550	0·6588	0·6631
2·5		7260		0·6342	
3·0			7420		0·6203
4·0			10 290		0·5896

The temperatures given for points on the Hugoniot curve would be helpful if they were not highly dependent upon somewhat arbitrary choices of constants, particularly heat capacity, and the neglect of latent heats of the various transformations. Some estimates are given in Table 2. These temperatures are more easily reconciled with the phase diagram of Fig. 2, the ' inside ' arrangement, than with Fig. 1, but in view of the uncertainties the argument is tenuous. Without new evidence, it appears to be unrealistic to claim that the melting temperature of iron, at core pressures, is known to within 500°.

Calculation of isentropes

Thermodynamics provides the basis for calculating reversible adiabatics or isentropes, in the relations:

$$(\partial T/\partial P)_S = T\alpha V/C_P = T\gamma/K_S;\ (\partial T/\partial V)_S = -T\gamma/V$$

where γ is the ' thermodynamic ' Gruneisen ratio ($= \alpha K_S V/C_P = \alpha K_T V/C_V$). Integration requires knowledge of the dependence of γ on T and V.

Relatively little is known about the behaviour of γ for liquid metals. Recent work on the velocity of sound in liquid sodium (Leibowitz, Chasanov & Blomquist 1971) shows γ, at 1 atmosphere, first rising, then falling, as temperature rises from 100 °C to 1000 °C, though remaining between 1·075 and 1·22. The same data show γ/V falling from 1·07 to 0·76 (g cm^{-3}) for this interval of temperature. Thus the usual assumption, reasonably well verified for a few solids, that γ or γ/V is independent of temperature, is not valid for liquid sodium.

The measurements of thermal expansion and heat capacity of liquid iron permit the calculation of $(\partial T/\partial P)_S$ at 1 atmosphere; with $T = 1808$ °K, $\rho = 7{\cdot}014$ g cm^{-3}, $\alpha = 119{\cdot}10^{-6}$ deg^{-1}, and $C_P = 0{\cdot}787$ Jg^{-1} deg^{-1}, the initial rate of rise for the isentrope is 3·9°/kb, slightly higher than $(dT/dP)_m$ for delta iron (Kirshenbaum & Cahill 1962; Hultgren *et al.* 1963). At 2000 °K, this becomes 4·5°/kb.

Little is known about the compressibility of liquid iron, though it is reasonable to suppose that it is greater than that of the solid phases along the melting curve, and that $(\partial T/\partial P)_S$ will decrease as pressure increases. In the $T-V$ plane, T increases as V decreases, and the positive ratio, $-(\partial T/\partial V)_S$ probably increases as V decreases. The details depend upon the behaviour of γ, unknown for the liquid, and uncertain for the γ and ε phases of iron. Even for α-iron, γ can be calculated only to 500 °C, the upper limit for the measurement of K_S (Leese & Lord 1968); the values are much affected by the abnormal increase of C_P as the magnetic transition is approached. At 1 atmosphere, γ falls from 1·68 to 25 °C, to 1·39 at 500 °C, and thus does not satisfy the basic assumption of independence of temperature (Table 3).

Table 3

Thermodynamic data for alpha iron, 1 *atmosphere*

T, °C	ρ g cm^{-3}	C_P J g^{-1} deg^{-1}	$10^6\,\alpha$ deg^{-1}	K_S kb	γ	$\gamma\rho$ g cm^{-3}
25	7·87	0·447	35	1690	1·68	13·2
100	7·85	0·474	37·8	1620	1·65	13·0
200	7·82	0·518	41·7	1570	1·62	12·7
300	7·78	0·567	45·0	1580	1·61	12·5
400	7·75	0·618	47·7	1500	1·49	11·5
500	7·71	0·669	48·6	1480	1·39	10·7
600	7·67	0·790	48	(1360)	(1·08)	8·3

Reference

Leese & Lord 1968; Hultgren *et al.* 1963; Pearson 1967.

With the common, but unverified, assumption that γ is independent of temperature, the temperatures and volumes on an isentrope are related according to

$$\ln T_2/T_1 = -\int_{V_1}^{V_2} \gamma dV/V$$

which may be integrated for various assumptions about the variation of γ with V. The simplest functional relation is of the form,

$$\gamma = \gamma_0(V/V_0)^n$$

where n is usually equal to or greater than 1 (see, for example, Bassett *et al.* 1968). Shock compression of iron gives no clear answer (McQueen *et al.* 1970, p. 327) though $n = 0$ appears to be excluded, while $n = 1$ is not.

These curves apply only to single phases; an isentrope passing through a phase boundary will be deflected, the direction depending upon the sign of the entropy change along the phase boundary, which is, of course, just what is in question. The entropy of the liquid is greater than that of the solid in equilibrium with it; if entropy increases as temperature increases along the phase boundaries, the continuation of an isentrope of the liquid which reaches the phase boundary must be toward a point on the solidus at a higher temperature, and vice versa. The release isentropes, and calculated entropies along the Hugoniot given by McQueen *et al.* (1970) and others, do not take the entropies of the phase changes into account, and the calculated temperatures on the Hugioniot are probably too high, but these calculations suggest that the change of entropy along the melting curve may be so small that crude estimates are inadequate to distinguish even the sign of the variation.

These different assumptions lead to appreciably different isentropes. For example, suppose that $\gamma = 1{\cdot}8$ for $V/V_0 = 1{\cdot}12$, and $T = 4850$ K at $V/V_0 = 0{\cdot}615$, as in Fig. 1. Isentropes emanating from this point, for $n = 0$, 1 and 2 are tabulated in Table 4. In the interesting region at about $V/V_0 = 0{\cdot}7$, which corresponds to a pressure of 1·5 to 2 Mb, the calculated temperature for $n = 0$ is 630° below that for $n = 2$, and nearly 400° below that for $n = 1$. One of the isentropes given by Higgins & Kennedy appears to be based on the assumption, $n = 0$, which gives the largest rate of decrease of temperature on expansion.

Table 4

Temperatures on isentropes for different exponents n

V/Vo		T, °K	
	$n = 0$	$n = 1$	$n = 2$
0·615	4850	4850	4850
0·65	4390	4586	4698
0·7	3842	4233	4476
0·8	3021	3607	4019
0·9	2444	3074	3558
1·0	2022	2619	3105
1·1	1703	2232	2670

The assumption, $n = 1$, is frequently made for the reduction of Hugoniot curves to isentropes or isotherms. Adopting this, we have $(\partial T/\partial V_S) = -T\gamma/V_0$. If, following Kraut & Kennedy, we suppose the melting temperature to be linear with volume, so that $T_m = A - BV/V_0$, the slopes of all isentropes will equal the slope of the melting line at a temperature, $T = B/\gamma_0$, and one isentrope will be tangent to the melting line at this temperature, at a volume $V/V_0 = A/B - 1/\gamma_0$. With the construction of Fig. 1, this tangent contact is at $V/V_0 = 0{\cdot}77$, and a pressure of about 1·2 Mb, somewhat below the pressure at the mantle–core boundary. The change of slope of the isentrope within the range of core pressures is, however, relatively small, and slight alterations of the various parameters can place the point of contact at smaller volumes and higher pressures.

If the epsilon phase is in equilibrium with the liquid at core pressures, as suggested by Fig. 2, then the isentropes of the liquid seem likely to be ' flatter ' than the melting curve; expansion of the liquid from the point at 3·4 Mb leaves it perhaps as much as 100° hotter than the melting temperature at 1·35 Mb. The smallness of these differences, in comparison with the large uncertainties of the estimates, leaves the relation of isentrope to melting curve indeterminate. The generally small difference between melting curve and isentrope has been pointed out by McQueen *et al.* (1971), who show examples of differences of both signs for metals having a single solid phase. The existence of the high-density epsilon phase of iron introduces an important factor, difficult to evaluate, but suggesting the likelihood of a significant departure from a single linear dependence of melting temperature on volume for the region of geophysical interest. It also makes improbable the ' abnormal ', caesium-like melting relations proposed by McLachlan & Ehlers (1971).

Geophysical application

We have now to consider the relevance of the iron phase diagram to the problem of the Earth's core. It has been recognized that iron is too dense to meet the requirements of the outer core (Birch 1952, 1964; MacDonald & Knopoff 1958; Knopoff & MacDonald 1960; McQueen *et al.* 1964) and of possible alloying elements, silicon and sulphur have been proposed as suitably abundant and likely to enter a phase composed mainly of iron. From the meteorite analogy, nickel is also a plausible component. Any element in small proportions would reduce the melting temperature below that of pure iron, and either silicon or sulphur might have relatively large effects. There is positive evidence that silicon–iron, with about 15 per cent silicon by weight, comes close to satisfying the requirements for the outer core. Balchan & Cowan (1966; see also Kormer & Funtikov 1965) have studied the shock compression of two-iron–silicon alloys to pressures of 2·7 Mb; and have calculated the sound velocity $(\partial K/\partial P)_S^{\frac{1}{2}}$ along several conventional isentropes ($n = 1$) for the alloy with 19·8 per cent silicon. One of these (their solution B) is shown in Fig. 3, where velocity is plotted versus density; also shown are calculated values by Dziewonski & Gilbert

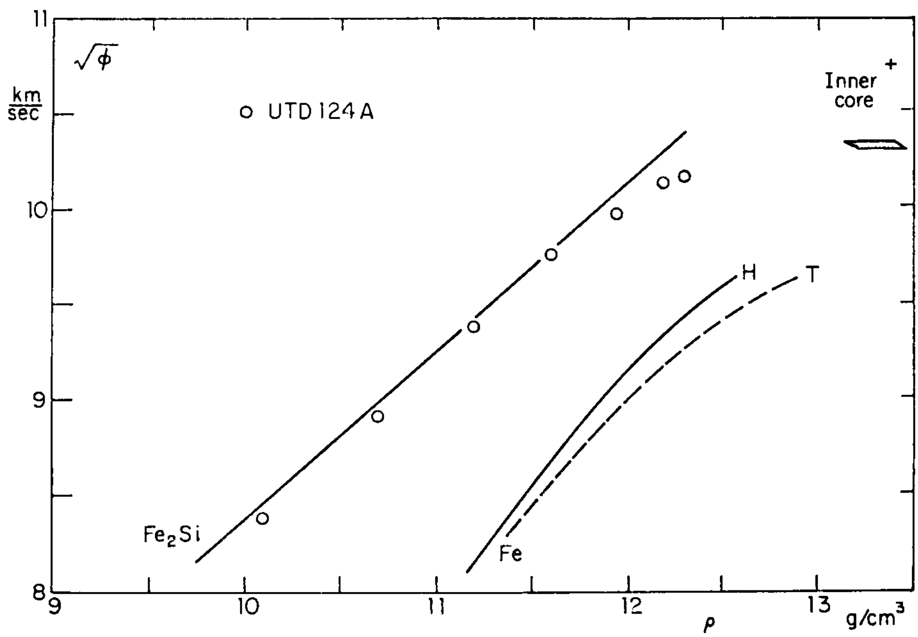

FIG. 3. Velocity of sound versus density, for an iron-silicon alloy (Balchan & Cowan 1966, 19·8 per cent silicon, isentrope 'B'), for iron (McQueen *et al.* 1970; H on Hugoniot, T on 293°K isotherm) and (circles) from the solution UTD 124A of Dziewonski & Gilbert (1972). Several estimates for the inner core are also shown.

(1972) for velocity and density in the core, based on free oscillations and seismic velocities. The close agreement of these independent studies supports the hypothesis that silicon alone, in a proportion of about 15 per cent by weight, accounts for the velocity–density relation in the outer core; that 19·8 per cent is too much is indicated by the density–pressure plot of Fig. 4, which shows the isotherm at 293 K for iron, and the density–pressure curve for the core. The density for the inner core is closer to the expectation for iron or iron–nickel with little or no light alloying element, and it seems plausible that the liquid outer core should contain more of the 'impurities' than the solid inner core. This in turn suggests that the temperature at the boundary between inner and outer core cannot exceed the melting temperature of iron at the pressure of 3·4 Mb, nor be less than the temperature required to melt the alloy. At 1 atmosphere, the reduction of the melting temperature of iron is about 330°, at the eutectic near 20 per cent silicon.

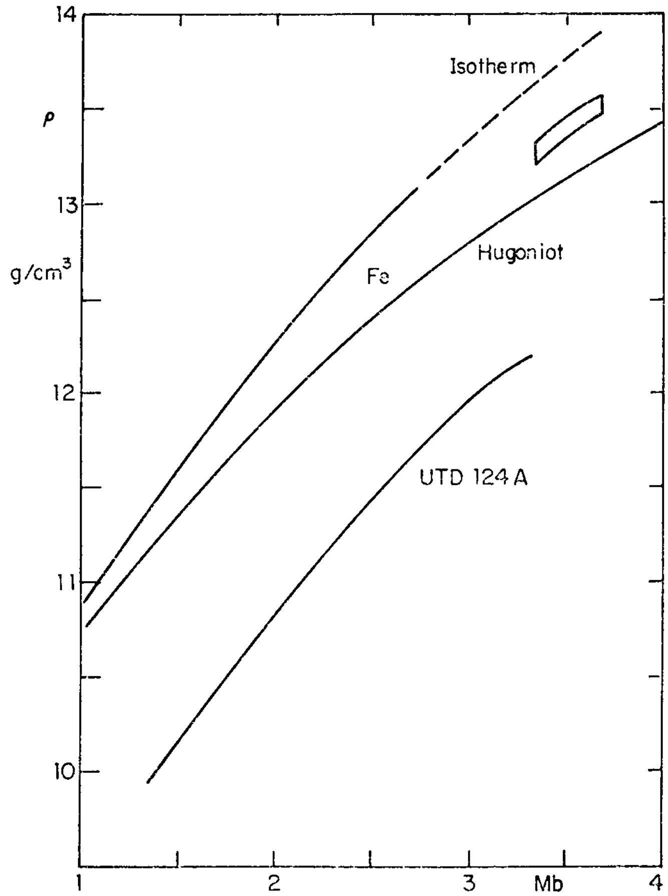

FIG. 4. Density versus pressure for iron and for the Earth (references as for Fig. 3). The corresponding curve for the 19·8 per cent silicon alloy lies about 0·3 g cm^3 below the UTD 124A curve. Rectangular area at upper right shows probable limits for the inner core.

The incorporation of so much silicon would, however, modify the phase diagram. Silicon enlarges the field of the alpha phase, with the displacement of the alpha-epsilon boundary toward higher pressures (Zukas *et al.* 1963); the gamma phase disappears, at 1 atmosphere, for silicon proportions exceeding about 3 per cent. The increase of the alpha-epsilon transition pressure is nearly linear with silicon content up to about 4·5 per cent, but thereafter appears to be more rapid, and the pressure conceivably could be as high as 1 Mb for the 19·8 per cent silicon alloy studied by Balchan & Cowan, who noticed a break in the $U_s - U_P$ plot at about this point. Nickel has little effect upon the alpha-epsilon transition, in proportions of geophysical interest (McQueen & Marsh 1966); manganese lowers the transition pressure (Christou & Brown 1971). It may be conjectured that in the iron–nickel–silicon system, which may be the simplest one with a reasonable resemblance to the core, the gamma phase either vanishes completely for the probable composition, or is restricted to pressures below those of the core. If the high-density epsilon phase is the solid phase in equilibrium with the liquid at core pressures, the general relations of Fig. 2 may still apply, though with reduced temperatures, and the isentrope corresponding to expansion from the boundary between inner and outer cores may again lie entirely in the liquid field, though never far from the freezing curve.

With melting curve and isentrope nearly coincident, departures from adiabatic conditions will be difficult to detect from rates of change of seismic velocity or density; examination of recent distributions (for example, Dziewonski & Gilbert 1972) derived from inversion of free oscillation periods, including many high order overtones, confirm a rise of density closely consistent with the Adams–Williamson rate. Some complications, still debated, in the seismic transition region between outer and inner cores, may reflect the existence of two-phase regions, such as might exist in a system of several components (Bolt 1964; Adams & Randall 1964; Buchbinder 1971).

Several authors have suggested that, in view of the subadiabatic temperatures proposed by Higgins & Kennedy, the outer core might consist of a ' slurry ' of solid particles in a liquid medium (Busse 1972; Malkus 1972). The reports of extremely low attenuation in the outer core (Engdahl 1968; Bolt & Qamar, 1970; Buchbinder 1971) seem qualitatively incompatible with such a constitution, but further examination of the question is needed.

As a more positive conclusion, estimates of 4000 °K for the mantle–core boundary, and 5000 °K for the central temperature, based on the phase diagram of iron, may have some standing as upper limits, with the temperatures in the real core perhaps no more than 1000° lower. These numbers are in reasonable agreement with many estimates based on other methods (for a compilation, see Birch 1963, p. 111).

Extrapolation in the temperature-volume plane, even if the phase boundaries are not exactly linear, may be less hazardous than extrapolation in the temperature-pressure plane, but we are still faced with large uncertainties concerning the initial slopes, and even worse, the nature of the phases of interest.

Hoffman Laboratory,
Harvard University,
Cambridge,
Massachusetts 02138

References

Adams, R. D. & Randall, M. J., 1964. The fine structure of the Earth's core, *Bull. seis. Soc. Am.*, **54,** 1299–1313.

Alsop, L. E., 1963. Free spheroidal vibrations of the earth at very long periods. Part II. Effect of rigidity of the inner core, *Bull. seism. Soc. Am.*, **53,** 503–515.

Al'tshuler, L. V., Krupnikov, K. K., Ledenev, B. N., Zhuchikin, V. I. & Brazhnik, M. I., 1958. Dynamic compressibility and equation of state of iron under high pressure, *Sov. Phys. JETP*, **7,** 606–614.

Al'tshuler, L. V., Bakanova, A. A. & Trunin, R. F., 1962. Shock adiabats and zero isotherms of seven metals at high pressures, *Sov. Phys. JETP*, **15,** 65–74.

Balchan, A. S. & Cowan, G. R., 1966. Shock compression of two iron-silicon alloys to 2·7 megabars, *J. geophys. Res.*, **71,** 3577–3588.

Bancroft, D., Peterson, E. L. & Minshall, S., 1956. Polymorphism of iron at high pressure, *J. appl. Phys.*, **27,** 291–298.

Bassett, W. A., Takahashi, T., Mao, H. & Weaver, J. S., 1968. Pressure-induced phase transformation in NaCl, *J. appl. Phys.*, **39,** 319–325.

Birch, F., 1940. The alpha-gamma transformation of iron at high pressures, and the problem of the Earth's magnetism, *Am. J. Sci.*, **238,** 192–211.

Birch, F., 1952. Elasticity and constitution of the Earth's interior, *J. geophys. Res.*, **57,** 227–286.

Birch, F., 1963. Some geophysical applications of high-pressure research, in *Solids Under Pressure*, edited by W. Paul and D. M. Warschauer, pp. 137–162, McGraw-Hill, New York.

Birch, F., 1964. Density and composition of mantle and core, *J. geophys. Res.*, **69,** 4377–4388.

Bolt, B. A., 1964. The velocity of seismic waves near the Earth's center, *Bull. seism. Soc. Am.*, **54,** 191–208.

Bolt, B. A. & Qamar, A., 1970. Upper bound to the density jump at the boundary of the Earth's inner core, *Nature* (*London*), **228,** 148–150.

Boyd, F. R. & England, J. L., 1963. The melting of iron at high pressures, *Carnegie Inst. Washington, Year.*, **62,** 134–137.

Buchbinder, G. G. R., 1971. A velocity structure of the Earth's core, *Bull. seism. Soc. Am.*, **61,** 429–456.

Bullard, E. & Gubbins, D., 1971. Geomagnetic dynamos in a stable core, *Nature* (*London*), **232,** 548–549.

Bullen, K. E., 1946. A hypothesis on compressibility at pressures of the order of a million atmospheres, *Nature* (*London*), **157,** 405.

Bullen, K. E., 1949. Compressibility pressure hypothesis of the Earth's interior, *Mon. Not. R. astr. Soc. Geophys. Suppl.*, **5,** 355–368.

Bullen, K. E., 1950. Theoretical travel-times of *S* waves in the Earth's inner core, *Mon. Not. R. astr. Soc. Geophys. Suppl.*, **6,** 125–128.

Bundy, F. P., 1965. Pressure-temperature phase diagram of iron to 200 kbar, 900°C, *J. appl. Phys.*, **36,** 616–620.

Bundy, F. P. & Strong, H. M., 1962. Behaviour of metals at high temperatures and pressures, in *Solid State Physics*, vol. 13, edited by F. Seitz and D. Turnbull, pp. 81–146, Academic press, New York.

Busse, F. H., 1972. Comments on Paper by G. Higgins and G. C. Kennedy, The Adiabatic gradient and the melting point gradient in the core of the Earth, *J. geophys. Res.*, **77,** 1589–1590.

Christou, A. & Brown, N., 1971. High-pressure Phase transition and demagnetization in shock compressed Fe-Mn alloys, *J. appl. Phys.*, **42,** 4160–4170.

Derr, J. S., 1969. Internal structure of the Earth inferred from free oscillations, *J. geophys. Res.*, **74,** 5202–5220.

Dziewonski, A. M., 1971. Overtones of free oscillations and the structure of the Earth's interior, *Science*, **1972,** 1336–1338.

Dziewonski, A. M. & Gilbert, F., 1971. Solidity of the inner core of the Earth inferred from normal mode observation, *Nature* (*London*), **234,** 465–466.

Dziewonski, A. M. & Gilbert, F., 1972. Observation of normal modes from 84 recordings of the Alaskan earthquake of 1964 March 28, *Geophys. J. R. astr. Soc.*, **27,** 393–446.

Engdahl, E. R., 1968. Seismic waves within Earth's outer core; multiple reflection, *Science*, **161,** 263–264.

Getting, I. C. & Kennedy, G. C., 1970. The effect of pressure on the emf of chromel-alumel and platinum-platinum 10% rhodium thermocouples, *J. appl. Phys.*, **41,** 4552–4562.

Giles, P. M., Logenbach, M. H. & Marder, A. R., 1971. High-pressure $\alpha \leftrightarrows \varepsilon$ martensitic transformation in iron, *J. appl. Phys.*, **42,** 4290–4295.

Higgins, G. & Kennedy, G. C., 1971. The adiabatic gradient and the melting point gradient in the core of the Earth, *J. geophys. Res.*, **76,** 1870–1878.

Hultgren, R., Orr, R. L., Anderson, P. D. & Kelley, K. K., 1963. *Selected Values of Thermodynamic Properties of Metals and Alloys*, p. 107, John Wiley and Sons, Inc., New York.

Jamieson, J. C. & Lawson, A. W., 1962. X-ray diffraction studies in the 100 kilobar pressure range, *J. appl. Phys.*, **33,** 776–780.

Johnson, P. C., Stein, B. A. & Davis, R. S., 1962. Temperature dependence of shock-induced phase transformations in iron, *J. appl. Phys.*, **33,** 557–561.

Jordan, T. H. & Franklin, J. N., 1971. Optimal solutions to a lunar inverse problem in geophysics, *Proc. Nat. Acad. Sci.*, **68**, 291–293.

Julian, B. R., Davies, D. & Sheppard, R. M., 1972. *PKJKP*, *Natue* (*London*), **235**, 317–318.

Kelley, K. K., 1949. Contributions to the data on theoretical metallurgy, X, High-temperature heat-content, heat-capacity, and entropy data for inorganic compounds, *U.S. Bur. Mines*, *Bull.* **476**, 85.

Kirshenbaum, A. D. & Cahill, J. A., 1962. The density of liquid iron from the melting point to 2500°K, *Trans. AIME*, **224**, 816–819.

Knopoff, L. & MacDonald, G. J. F., 1960. An equation of state for the core of the Earth, *Geophys. J. R. astr. Soc.*,**3**, 68–77.

Kormer, S. B. & Funtikov, A. I., 1965. A study of impact compression of ferrosilicon and a possible composition of the Earth's core, *Izv. Acad. Sci. U.S.S.R. Phys. Solid Earth*, *No.* **5**, 285–286.

Kraut, E. A. & Kennedy, G. C., 1966. New melting law at high pressure, *Phys. Rev.*, **151**, 668–675.

Leese, J. & Lord, A. E., 1968. Elastic stiffness coefficients of single crystal iron from room temperature to 500°C, *J. appl. Phys.*, **39**, 3986–3988.

Lehmann, I., 1936. P′, *Union Geod. Geophys. Int.*, *Assoc. Seism.*, *Ser. A.*, *Travaux Scientifiques*, *No.* **14**, 87–115.

Leibowitz, L., Chasanov, M. G. & Blomquist, R., 1971. Speed of Sound in Liquid Sodium to 1000°C, *J. appl. Phys.*, **42**, 2135–2137.

Macdonald, G. J. F. & Knopoff, L., 1958. On the chemical composition of the outer core, *Geophys. J. R. astr. Soc.*, **1**, 284–297.

Malkus, W. V. R., 1972. Convection at the melting point, a thermal history of the earth's core, *J. geophys. Fluid Dyn.*, in press.

Mao, H., Bassett, W. A. & Takahashi, T., 1967. Effect of pressure on crystal structure and lattice parameters of iron up to 300 kbar, *J. appl. Phys.*, **38**, 272–276.

McLachlan, D. & Ehlers, E. G., 1971. Effect of pressure on the melting temperature of metals, *J. geophys. Res.*, **76**, 2780–2789.

McQueen, R. G. & Marsh, S. P. Equation of state for nineteen metallic elements from shock-wave measurements to two megabars, *J. appl. Phys.*, **31**, 1253–1269, 1960.

McQueen, R. G., Fritz, J. N. & Marsh, S. P., 1964. On the composition of the Earth's interior, *J. geophys. Res.*, **69**, 2947–2965.

McQueen, R. G. & Marsh, S. P., 1966. Shock-wave compression of iron-nickel alloys and the Earth's core, *J. geophys. Res.*, **71**, 1751–1756.

McQueen, R. G., Marsh, S. P., Taylor, J. W., Fritz, J. N. & Carter, W. J., 1970. The equation of state of solids from shock wave studies, in *High Velocity Impact Phenomena*, pp. 293–568, Academic Press, Inc., New York.

McQueen, R. G., Carter, W. J., Fritz, J. N. & Marsh, S. P., 1971. The solid-liquid phase line in Cu in *Accurate Characterization of the High Pressure Environment*, edited by E. C. Lloyd, p. 326, Nat. Bur. Stand. Special Publ. 326.

Pearson, W. B., 1967. *A Handbook of Lattice Spacings and Structure of Metals and Alloys*, *Vol.* 4, Pergamon Press Inc., New York.

Pekeris, C. L., Alterman, Z. & Jarosch, H., 1962. Effect of the rigidity of the inner core on the fundamental oscillation of the Earth, *Proc. Nat. Acad. Sci.*, **48**, 592–595.

Ramsey, W. H., 1950. On the compressibility of the Earth, *Mon. Not. R. astr. Soc. Geophys. Suppl.*, **6**, 42–49.

Sterrett, K. F., Klement, W. & Kennedy, G. C., 1965. Effect of pressure on the melting of iron, *J. geophys. Res.*, **70**, 1979–1984.

Strong, H. M., 1959. The experimental fusion curve of iron to 96 000 atmospheres, *J. geophys. Res.*, **64**, 653–659.

Strong, H. M., 1961. Melting and other phase transformations at high pressure in *Progress in Very High Pressure Research*, edited by F. P. Bundy, W, R. Hibbard, and H. M. Strong, pp. 182–193, John Wiley, New York.

Takahashi, T. & Bassett, W. A., 1964. High-pressure polymorph of iron, *Science*, **145**, 483–486.

Takahashi, T. & Bassett, W. A., 1965. The composition of the Earth's interior, *Sci. Amer.*, **212**, 100, 108.

Zukas, E. G., Fowler, C. M., Minshall, F. S. & O'Rourke, J. O., 1963. The behaviour of iron-silicon alloys under impulsive loading, *Trans. AIME*, **227**, 746–753.