

Volume Dependence of Melting Temperature at High Pressure and its Relation to a New Dimensionless Quantity¹⁾

Die Volumenabhängigkeit der Schmelztemperatur für hohe Drücke und ihre Beziehung zu einer neuen dimensionslosen Größe

Зависимость температуры плавления от атомного объема при высоких давлениях и новая безразмерная величина

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Abstract

The dependence of melting temperature on the atomic volume is inferred in two separate ways from different assumptions. The first deduction is based on an interatomic pair potential and a dislocation model, while the second one is based on the equation of state by ULLMANN and PAN'KOV, on an expression for the dependence of the GRÜNEISEN ratio on pressure and bulk modulus and on LINDEMANN'S law. It is also possible to infer the equation of state from the lattice theory alone. From this, the exponents of the $T_m(v)$ equations are independently determined. They are found to be in agreement. Reversing the sequence of conclusions, one may, if one accepts the other aforementioned premises, infer LINDEMANN'S law. However, this applies only for high coordination numbers and high pressures, respectively. In a systematic manner, new dimensionless quantities Q_j containing the melting temperature are defined, and their pressure dependence is calculated analytically and numerically, there being no necessity of solving the equation of state so that density stands alone on one side of equality. The most simple one of these dimensionless quantities, Q_0 , shows an interesting systematic for the elements of the periodic table. For high pressures, the Q_0 values of the metals are scattered around merely insignificantly variable average values which slightly depend on pressure. If one might proceed from the assumption that, at an appropriate pressure, but at an assumed zero temperature, the materials of the Earth's core would exist in the form of a close-packed structure, it is possible to determine the ratio of melting temperature to formula weight as a function of the pressure for the actual Earth's core.

Zusammenfassung

Die Abhängigkeit der Schmelztemperatur T_m vom Atomvolumen v wird auf zwei getrennten Wegen aus unterschiedlichen Voraussetzungen hergeleitet. Die erste Herleitung geht von einem zwischenatomaren Potential und einem Versetzungsmodell aus, die zweite beruht auf der Zustandsgleichung von ULLMANN und PAN'KOV, auf der Vashchenko-Zubarev-Formel für die Abhängigkeit des Grüneisen-Verhältnisses von Druck und Inkompressibilität und auf LINDEMANN'S Schmelzpunktgesetz. Aus der Gittertheorie allein kann man auch eine Zustandsgleichung herleiten. Aus den beiden Zustandsgleichungen werden unabhängig die Exponenten der T_m - v -Gleichungen bestimmt. Diese erweisen sich als übereinstimmend. In Umkehrung der Schlußkette kann man bei Annahme der anderen Voraussetzungen das Lindemann-Gesetz herleiten, was jedoch mit Notwendigkeit nur für hohe Koordinationszahlen bzw. hohe Drücke gilt. Es werden in systematischer Weise neue dimensionslose Größen Q_j , die die Schmelztemperatur enthalten, definiert und ihre Druckabhängigkeit analytisch und numerisch berechnet, wobei Auflösbarkeit der dabei benutzten Zustandsgleichung nach der Dichte nicht nötig ist. Die einfachste dieser dimensionslosen Größen, Q_0 , zeigt für die Elemente im Periodensystem eine interessante Systematik. Für hohe Drücke streuen die Q_0 -Werte der Metalle um nur wenig veränderliche Mittelwerte, die schwach vom Druck abhängen. Falls man annimmt, daß die Stoffe des Erdkerns unter entsprechendem Druck bei (gedachter) Nulltemperatur in dichtester Kugelpackung vorlägen, so ergibt sich eine Möglichkeit, das Verhältnis von Schmelztemperatur zu Formelgewicht als Funktion des Druckes für den Erdkern zu bestimmen.

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1. Introduction

The problem of the dependence of the melting temperature T_m on pressure P has neither theoretically nor experimentally been satisfactorily solved for the high pressures of the lower mantle and the Earth's core. That is to say that the published melting point curves vary considerably from author to author in contrast to the modern pressure-dependence curves of density, bulk modulus, shear modulus and seismic velocities. However, it is precisely this quantity which is decisive for various fundamental problems of geodynamics, e.g., for mantle convection and for the magneto-hydrodynamic theory of the outer core. The reason is that, firstly, viscosity — irrespective of the prevailing creep mechanism — is proportional to $\exp(k_2 T_m/T)$, with k_2 being a constant and T the actual temperature, and, secondly, that the mutual positions of the curves of adiabatic temperature, melting temperature, conduction temperature and actual temperature are decisive for the dynamo mechanism (see KENNEDY and HIGGINS [23], LOPER [30], ULLMANN and WALZER [48, 49]). The problem of the actual melting temperature curve of the outer core can be formally subdivided into three questions: a) Which theory for $T_m(P)$ applies to pure materials under such high pressures? b) What is the chemical composition of the core? c) How do the phase diagrams of probable mixtures vary with pressure? The present paper is designed to make a contribution to question a).

2. A new approach to Lindemann's law

Below, it will be shown that it is possible to approach in two separate ways the same law for the dependence of melting temperature on volume, which applies to pressures as prevailing in the interior of planets.

The *first deduction* is based on the lattice theory and on a dislocation model. We assume that for pressures in the deep interior of the Earth an atom (or molecule) will mostly have twelve adjacent neighbours. Therefore, in the following we shall always consider a face centered cubic lattice (see Fig. 1). We suppose that our considerations apply with minor changes also to other lattices having a high coordination number. The volume per number of atoms is $v = a^3/4$, the neighbour distance $r_0 = a/\sqrt{2}$. Lattice points can be expressed as $l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3$, with $|\mathbf{a}_1| = |\mathbf{a}_2| = |\mathbf{a}_3| = r_0$ and l_1, l_2 and l_3 being integers. For fcc, $l_1 + l_2 + l_3$ must be an even integer. Moreover, we define

$$l^2 = l_1^2 + l_2^2 + l_3^2. \quad (1)$$

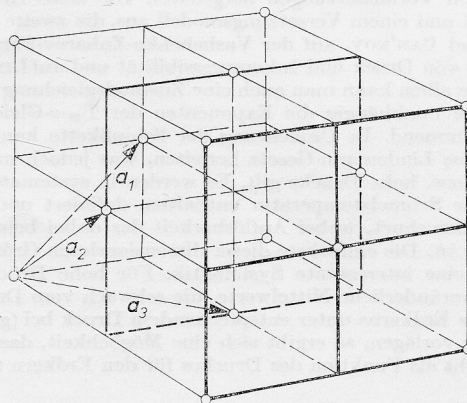


Fig. 1. The fcc lattice

According to BORN and HUANG [5] we assume that the interatomic forces have the following potential:

$$\psi(r^2) = u_0 \frac{mn}{m-n} \left\{ \frac{1}{m} \left(\frac{\varrho_0}{r} \right)^m - \frac{1}{n} \left(\frac{\varrho_0}{r} \right)^n \right\} \quad (2)$$

where $m > n$. The minimum of the potential function ψ has the value $-u_0$ and is located at a distance ϱ_0 (see Fig. 2). For cubic BRAVAIS lattices, there are three independent elastic constants: c_{11} , c_{12} , c_{44} . Because of the CAUCHY relation for the central force we have, additionally, $c_{12} = c_{44}$. From Eq. (2), we obtain for the elastic constants:

$$c_{11} = \frac{u_0}{2} \cdot \frac{mn}{m-n} \left\{ (m+2) \left(\frac{\varrho_0}{4^{1/3}} \right)^m v^{-(m/3+1)} \Sigma \frac{l_1^4}{l^{m+4}} - (n+2) \left(\frac{\varrho_0}{4^{1/3}} \right)^n v^{-(n/3+1)} \Sigma \frac{l_1^4}{l^{n+4}} \right\}, \quad (3)$$

$$c_{12} = \frac{u_0}{2} \cdot \frac{mn}{m-n} \left\{ (m+2) \left(\frac{\varrho_0}{4^{1/3}} \right)^m v^{-(m/3+1)} \Sigma \frac{l_1^2 l_2^2}{l^{m+4}} - (n+2) \left(\frac{\varrho_0}{4^{1/3}} \right)^n v^{-(n/3+1)} \Sigma \frac{l_1^2 l_2^2}{l^{n+4}} \right\}. \quad (4)$$

The summation has to be performed over all lattice points. The averaged isotropic shear modulus μ is

$$\mu = \frac{1}{5} (c_{11} - c_{12} + 3c_{44}). \quad (5)$$

This is VOIGT's formula. From Eqs. (3) ... (5) and CAUCHY's relation it follows that

$$\mu = \frac{u_0}{10} \cdot \frac{mn}{m-n} \{ c_1 v^{-(m/3+1)} - c_2 v^{-(n/3+1)} \} \quad (6)$$

where

$$c_1 = \left(\Sigma \frac{l_1^4}{l^{m+4}} + 2 \Sigma \frac{l_1^2 l_2^2}{l^{m+4}} \right) (m+2) \left(\frac{\varrho_0}{4^{1/3}} \right)^m \quad (7)$$

and

$$c_2 = \left(\Sigma \frac{l_1^4}{l^{n+4}} + 2 \Sigma \frac{l_1^2 l_2^2}{l^{n+4}} \right) (n+2) \left(\frac{\varrho_0}{4^{1/3}} \right)^n. \quad (8)$$

For a perfect crystal and our potential function (2), we have the following enthalpy H :

$$H = \frac{N}{2} u_0 \frac{mn}{m-n} \left\{ \frac{\varrho_0^m}{m} 2m/3 \left(\Sigma \frac{1}{l^m} \right) v^{-m/3} - \frac{\varrho_0^n}{n} 2n/3 \left(\Sigma \frac{1}{l^n} \right) v^{-n/3} \right\} + PNv. \quad (9)$$

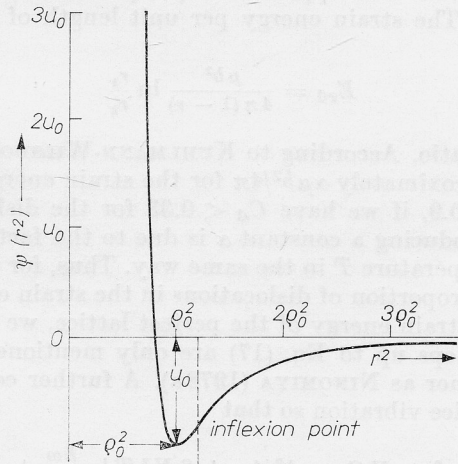


Fig. 2. The potential function $\psi(r^2)$ according to BORN and HUANG [5]

N is the number of atoms or molecules. From the general thermodynamic relations $H = E + PV$ and $P = -(\partial E/\partial V)_S$ we obtain for an elastic compression $\partial H/\partial v = 0$. E is the internal energy, P the pressure, V the volume, v , as before, the atomic volume. Index S means isentropic. The equation of state results from Eq. (9) and $\partial H/\partial v = 0$.

$$P = \frac{u_0}{6} \cdot \frac{mn}{m-n} \left\{ 2^{m/3} \varrho_0^m \left(\sum \frac{1}{l^m} \right) v^{-(m/3+1)} - 2^{n/3} \varrho_0^n \left(\sum \frac{1}{l^n} \right) v^{-(n/3+1)} \right\}. \quad (10)$$

The bulk modulus κ is obtained from this and from $\kappa = -v \, dP/dv$.

$$\kappa = \frac{u_0}{18} \cdot \frac{mn}{m-n} \{ c_3 v^{-(m/3+1)} - c_4 v^{-(n/3+1)} \} \quad (11)$$

where

$$c_3 = 2^{m/3} \varrho_0^m \left(\sum \frac{1}{l^m} \right) (m+3) \quad (12)$$

and

$$c_4 = 2^{n/3} \varrho_0^n \left(\sum \frac{1}{l^n} \right) (n+3). \quad (13)$$

So far, we have used the theory of the perfect lattice for determining quantities which we are going to employ now in a dislocation theory of melting. Like MACKENZIE and MOTT [32], KUHLMANN-WILSDORF [26], STACEY and IRVINE [44], NINOMIYA [36] and others we assume that the free energy of dislocations becomes zero at the melting point and that the dislocation concentration C_d reaches a saturation value. COTTERILL [10,11] gives an excellent presentation of the relationship between melting, dislocations, anharmonicity, solitons and other phenomena. The basic idea presented below is that the number of dislocations increases so rapidly as the melting point is approached that the shear modulus nearly decreases to zero.

The strain energy per unit length of a screw dislocation can be expressed by

$$E_{sc} = \frac{\mu b^2}{4\pi} \ln \frac{r_1}{r_2} \quad (14)$$

where b is the BURGERS vector. r_1 and r_2 are the outer and inner cutoff radii of the dislocation. The inner radius denotes the region of distortions in the core of the dislocation, the outer radius is approximately equal to the distance between two adjacent dislocations. The strain energy per unit length of an edge dislocation is given by

$$E_{ed} = \frac{\mu b^2}{4\pi(1-\nu)} \ln \frac{r_1}{r_2} \quad (15)$$

where ν is POISSON'S ratio. According to KUHLMANN-WILSDORF [26] and NINOMIYA [36], one may use approximately $\alpha \mu b^2/4\pi$ for the strain energy per unit length of a dislocation, with $\alpha \approx 0.9$, if we have $C_d < 0.33$ for the dislocation concentration. The possibility of introducing a constant α is due to the fact that r_1 and r_2 depend on pressure P and temperature T in the same way. Thus, for the dislocation density NC_d , there follows a proportion of dislocations in the strain energy of $NC_d \alpha \mu b^3/4\pi$. If we add to this the strain energy of the perfect lattice, we obtain the total strain energy. The further steps up to Eq. (17) are only mentioned because we proceed here in the same manner as NINOMIYA (1978a). A further contribution to the free energy stems from lattice vibration so that

$$G = \frac{1}{2} N v \kappa \varepsilon^2 + NC_d \alpha \mu b^3/4\pi + 3NkT \ln \frac{\hbar\omega}{kT} + NC_d kT \ln \lambda \quad (16)$$

results for the free energy. The last two terms describe the vibration free energy, ε is the uniform dilatation of the lattice, k the BOLTZMANN constant, ω the average frequency of phonons, $\lambda\omega$ the average frequency of dislocation vibration, \hbar PLANCK's constant. From Eq. (16) we obtain

$$G = G_0 + N\alpha v \left[\frac{1}{4\pi} \left(\frac{r_0^3}{v} \right) \alpha C_d \frac{\mu}{\alpha} - \frac{1}{2} \varepsilon_d^2 \right] - NkT \left[3\varepsilon_d\gamma + C_d \ln \frac{1}{\lambda} \right]. \quad (17)$$

This formula is now the starting point for our further considerations. G_0 is the free energy of the perfect lattice, γ is GRÜNEISEN's ratio. At the melting point, the free energy of dislocations vanishes, i.e., $G - G_0 = 0$ applies. ε_d may be assumed to be approximately constant because the relative volume change on melting is approximately constant for the chemical elements, deviations from the mean value being smallest for fcc, bcc and hep structures (GSCHNEIDNER [17]). Now let us apply the melting point theory — as can be seen below — to elements under high pressures so that these assumptions exactly apply. For fcc lattices, we have $r_0^3/v = \sqrt{2}$. Hence, from this, from $G - G_0 = 0$ and from Eqs. (6), (11), (17):

$$T_m = \frac{N}{\Delta S} \left[\frac{\sqrt{2}}{4\pi} \alpha C_d \frac{u_0}{10} \cdot \frac{mn}{m-n} (c_1 v^{-m/3} - c_2 v^{-n/3}) - \frac{1}{2} \varepsilon_d^2 \frac{u_0}{18} \cdot \frac{mn}{m-n} (c_3 v^{-m/3} - c_4 v^{-n/3}) \right] \quad (18)$$

the fusion entropy being expressed by

$$\Delta S = Nk [3\varepsilon_d\gamma + C_d \ln(1/\lambda)]. \quad (19)$$

Eq. (18) does not contain any essential implicate dependencies on v . In particular, ΔS is also approximately independent of $P(v)$ (GSCHNEIDNER [17]; STISHOV [45]). JACKSON [21], too, found that the fusion entropy is mainly a function of crystal structure. But the structure is considered to be invariable in our calculation. From Eq. (18) we obtain

$$T_m = \frac{N}{\Delta S} \cdot \frac{u_0}{4} \cdot \frac{mn}{m-n} (c_5 v^{-m/3} - c_6 v^{-n/3}) \quad (20)$$

where

$$c_5 = \frac{\sqrt{2}}{10\pi} \alpha C_d c_1 - \frac{\varepsilon_d^2}{9} c_3 \quad (21)$$

and

$$c_6 = \frac{\sqrt{2}}{10\pi} \alpha C_d c_2 - \frac{\varepsilon_d^2}{9} c_4. \quad (22)$$

Irrespective of the calculations made so far, Eq. (20) will now be derived from three completely different initial equations. Two of these initial equations have already been confirmed, the third one is LINDEMANN's law in the form of a differential equation. It can be shown that the sequence of conclusions can be reversed so that it is possible to infer from the first two initial equations of the following *second deduction* of Eq. (20) and from Eq. (20) to LINDEMANN's law. However, with the assumptions made by us, this is only a good approximation for high pressures. Like MATSUDA and HIWATARI [35], we suppose that the melting temperature depression observed for low pressures with Ge, Ga, Sb, Bi and ice is due to the loose packed structure of the solid. For high coordination numbers Eq. (20) must apply as has been shown above.

The first initial equation mentioned is the equation of state (model 1) by ULLMANN and PAN'KOV [47]

$$P = -\frac{3\kappa_0}{2-\kappa_1} (x^{(1/3)-(2/3)\kappa_1} - x^{-(1/3)-(1/3)\kappa_1}), \quad (23)$$

where $x = V/V_0 = v/v_0$. Index 0 denotes the corresponding quantity for $P = 0$. $\kappa_0 = \kappa|_{P=0}$ and $\kappa_1 = \left. \frac{\partial \kappa}{\partial P} \right|_{P=0}$, i.e., κ_0 denotes the zero pressure bulk modulus, κ_1 the first derivation of the bulk modulus at vanishing pressure. For $\kappa_1 = 4$, Eq. (23) becomes the equation of state by BIRCH [4]. WALZER, ULLMANN and PAN'KOV [52] compared Eq. (23) with other modern equations of state. They found that the equation yields results that show the best agreement with experimental high-compression data of cubic solids. The second initial equation is the expression obtained by VASHCHENKO and ZUBAREV [50] from the free volume theory for the GRÜNEISEN parameter:

$$\gamma = \frac{\frac{1}{2} \frac{d\kappa}{dP} - \frac{5}{6} + \frac{2}{9} \frac{P}{\kappa}}{1 - \frac{4}{3} \frac{P}{\kappa}}. \quad (24)$$

Using a new approach, IRVINE and STACEY [19] set up Eq. (24) for purely central forces, ignoring for the most part the special form of the interatomic potential. If, unrealistically, only one-dimensional atomic motion of the atoms is assumed, one obtains through the same method the well-known expression for γ suggested by DUGDALE and MACDONALD [12]. ULLMANN and WALZER [49] took into account the contribution of the electrons to γ , which, however, is not very significant for some applications. We have also shown that Eqs. (23) and (24) yield

$$\gamma = \frac{\kappa_1 - 1}{3} + \frac{1}{6} \frac{(\kappa_1 - 2)(\kappa_1 - 3)}{(2\kappa_1 - 5)x^{(2/3)-(1/3)\kappa_1} - \kappa_1 + 3}. \quad (25)$$

The third initial equation is LINDEMANN's melting law

$$T_m^{-1} dT_m/dP = 2 \left(\gamma - \frac{1}{3} \right) / \kappa, \quad (26)$$

where T_m is the melting temperature. A thermodynamic approach to LINDEMANN's law can be found with STACEY and IRVINE [43]. With $\kappa = -x dP/dx$, we obtain from Eq. (26)

$$\frac{d \ln T_m}{d \ln x} = 2 \left(\frac{1}{3} - \gamma \right). \quad (27)$$

Now, Eq. (25) is substituted in Eq. (27). Using the substitutions $T_m = e^\tau$ and $x = e^\xi$, one may solve the differential equation without neglects:

$$\tau(\xi) = \frac{2-\kappa_1}{3} \xi + \ln \left(\frac{2\kappa_1-5}{\kappa_1-3} \exp [((2/3) - (1/3)\kappa_1) \xi] - 1 \right) + \text{const}_1. \quad (28)$$

Hence,

$$T_m = \text{const} \cdot \left[\frac{2\kappa_1-5}{\kappa_1-3} \left(\frac{v}{v_0} \right)^{(4/3)-(2/3)\kappa_1} - \left(\frac{v}{v_0} \right)^{(2/3)-(1/3)\kappa_1} \right]. \quad (29)$$

It is immediately evident that Eq. (20) and Eq. (29) have the same mathematical form of $T_m = T_m(v)$. Now, let us compare the exponents. To be able to determine them by a second method, we compare the equation of state (10) derived solely from the lattice theory (without using the dislocation theory), with the equation of state

(23) for the derivation of which neither the VASHCHENKO-ZUBAREV formula nor LINDEMANN's law is required. When equating corresponding exponents in the two equations of state, we obtain

$$m = 2\kappa_1 - 4 \text{ and } n = \kappa_1 - 2. \quad (30)$$

Whereas the κ_1 for metals are found approximately in the range between 2.5 and 6.5, they are higher for inert gases. For instance, according to BIRCH [4], Ne has $\kappa_1 = 8.3$, consequently, we have $m = 12.6$ and $n = 6.3$. Thus, Eq. (2) yields nearly a 12—6 LENNARD-JONES potential for Ne. Generally (i.e., for all materials), $m = 2n$. If we substitute Eqs. (30) in Eq. (20), we can see that the exponents are in complete agreement with those of Eq. (29). As has already been pointed out in the remarks under Eq. (22), this agreement is a renewed proof of LINDEMANN's melting equation for high pressures if the other assumptions are accepted.

3. Discussion

LINDEMANN [28] supposed that melting starts when adjacent atoms get into direct contact through thermal vibration so that the crystal lattice is destroyed. GILVARRY [15] modified this conception by suggesting that the root-mean-square amplitude of thermal vibration must reach a certain percentage of the nearest-neighbour distance. MARTIN and O'CONNOR [34] measured these amplitudes by the separation of the elastic component of BRAGG diffraction peaks using the MÖSSBAUER effect. The substances used for their investigation were simple alkali halide and metal crystals. They found a good agreement with LINDEMANN's law. The version of LINDEMANN's law used in Eq. (26) can be traced back to GILVARRY [15]. For melting, the GIBBS free energies of the solid and of the fluid must be identical. This makes it easily possible, as is well known, to infer the CLAUSIUS-CLAPEYRON relationship by using the first law of thermodynamics. From this relationship and from the MIE-GRÜNEISEN equation, STACEY and IRVINE [43], using the thermodynamic approach, obtained a relation which differs from Eq. (26) only in that $1/3$ was substituted by 0.23 . Based on EYRING's significant-structure theory and on the above-mentioned identity of GIBBS free energies, LEPPALUOTO [27] obtained estimates for the melting temperatures of iron which correspond to the pressures existing in the outer core. They proved to be consistent with the LINDEMANN law. BOSCHI [6] published a paper on the topic discussed. His $T_m - P$ curve for Fe is similar to that attained by LEPPALUOTO, although it had been calculated using a different method.

Some substances show maxima in their melting curves, e.g., rubidium according to BUNDY [9], tellurium according to TIKHOMIROVA and STISHOV [46], sulfur according to VEZZOLI and WALSH [51]. These examples do not contradict the validity of LINDEMANN's law at high pressure, since each of the minima of the melting curve is a triple point where the $P - T$ regions of a less densely packed solid phase are bordering on a denser one. This shows that our presumption that a close-packed structure exists is not yet satisfied in this pressure range. Various attempts have been made to calculate theoretically melting curve maximum phenomena (e.g., OGURA et al. [38]; BRINDEAU et al. [8]), the assumptions being made frequently differing strongly from one another. It may very well be theoretically expected that many highly compressible substances exhibit experimental T_m -values in the pressure range currently accessible through static experiments, which are lower than the values calculated according to LINDEMANN's law. However, in view of the theory presented above it is not recommendable to extrapolate from the empirical linear $T_m - P$ relationship by KRAUT and KENNEDY [25] to the pressures prevailing in the Earth's core. Due to the fact that the chemical composition of the Earth's core has not been

completely determined yet (see, e.g., BRETT [7]; ITO [20]; RINGWOOD [40]; AHRENS [1]), it is impossible at present to specify a binding actual $T_m - P$ curve for the Earth's core. In spite of the rejection of the extrapolation according to KENNEDY and HIGGINS [23], however, the core paradox has not been resolved by any means. It has, namely, been found [49] that, if one additionally takes into account the small share in the GRÜNEISEN parameter, which is due to the electrons, the gradient of the adiabatic temperature is somewhat higher than that of the melting curve of hcp iron according to LIU [29]. However, IRVINE and STACEY concluded from equation-of-state studies that fcc iron is present in the core (STACEY [42]). Incidentally, if one uses only the VASHCHENKO-ZUBAREV gamma for calculating the adiabatic temperature, the paradox disappears also with LIU's melting curve. To attain greater accuracy in determining the melting point curve, surely, one will have to take into account the influence of the lighter components of the outer core. The phase diagram may really be very complicated. At present, there are no means for computing it with sufficient accuracy for these pressures. The assumption itself suggests that both the melting temperature and its gradient are lower than for pure substances. However, I am very confident that for pure substances, including iron, the previously deduced volume dependence of melting temperature or LINDEMANN's law under high pressures (and, thus, also for the Earth's core) is a good approximation.

4. A new dimensionless quantity and its pressure dependence

Let us now look for dimensionless quantities to be used as a tool for a subsequent numerical determination of the $T_m - P$ curve for the Earth's outer core, and for a discussion about the possible chemical composition of the outer core. The quantities are to differ as little as possible for various substances. In the construction, three premises have to be taken into account: Firstly, melting temperature is to be one of the initial quantities. Secondly, although we start by examining the dimensionless quantity for pure substances only (the chemical elements and some simple compounds), the measured quantities used are to be, as far as possible, such quantities as are quite reliably known also for the Earth as a function of depth. Thirdly, the pressure dependence of the measured quantities used must be considered, for which purpose we use the results achieved in the previous paragraphs. In view of the second premise, one may not simply take the LEIBFRIED number or BRAGG number (see GSCHNEIDNER [17]), because it contains the shear modulus. The shear modulus reduced to zero temperature cannot, however, be determined for the outer core, so that subsequent application to the outer core would not be possible. Now, to get a first hint, let us have a look at Fig. 3 where, using the data from Tab. 1, the melting temperature of the chemical elements has been plotted versus the bulk modulus for $P = 0$. The coordination number was taken from PLENDL and GIELISSE [39]. Although the points are widely scattered, the distribution of the points justifies the assumption that T_m/κ must be present in the expression we are looking for.

We define dimensionless quantities Q_j by

$$Q_j = N_1^{-1} \gamma^j \quad (31)$$

where j is a real number, and

$$N_1 = \frac{F}{R_0} \cdot \frac{\kappa}{T_m \rho} \quad (32)$$

F is the formula weight, ρ the density, R_0 the universal gas constant. The reason why the quantities Q_j have been formed precisely in this manner has been mentioned above and is to be discussed in greater detail in another paper. Here, we wish to study the dependence of these quantities on pressure, with the figures mainly showing

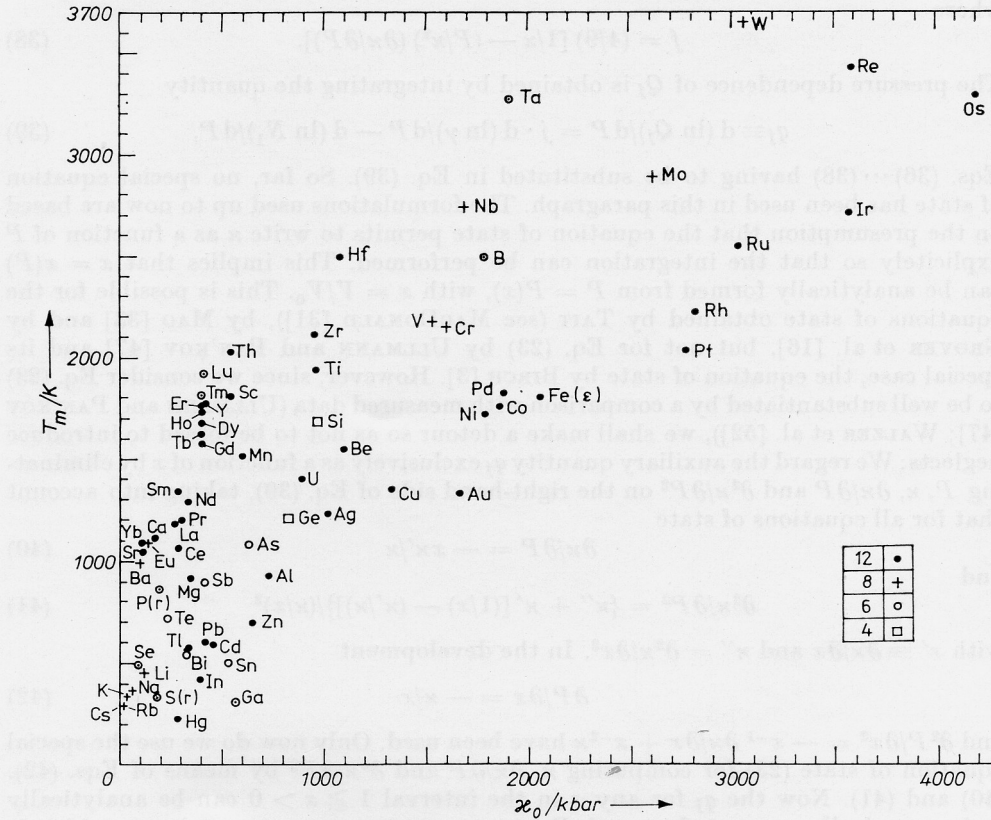


Fig. 3. Melting temperatures of the chemical elements plotted versus the bulk modulus for $P = 0$. The symbols denote the atomic coordination number. The legend can be seen at the lower right of the Figure

the results for $Q_0 = N_1^{-1}$. From Eq. (32) we obtain

$$d(\ln N_1)/dP = \partial(\ln \kappa)/\partial P - \partial(\ln T_m)/\partial P - \partial(\ln \varrho)/\partial P. \quad (33)$$

From this and from LINDEMANN's law, Eq. (26), follows

$$d(\ln N_1)/dP = \left[\partial \kappa / \partial P - 2 \left(\gamma - \frac{1}{3} \right) - (\kappa / \varrho) (\partial \varrho / \partial P) \right] / \kappa. \quad (34)$$

Since $\kappa = \varrho \partial P / \partial \varrho$ we have

$$d(\ln N_1)/dP = (\partial \kappa / \partial P - 2\gamma - 1/3) / \kappa. \quad (35)$$

From this and from Eq. (24) we obtain

$$\frac{d \ln N_1}{dP} = \frac{1 - (P/\kappa) (\partial \kappa / \partial P)}{(3/4) \kappa - P}. \quad (36)$$

Now we form the analogue to this equation for γ , using Eq. (24)

$$\frac{d \ln \gamma}{dP} = \frac{\partial^2 \kappa / \partial P^2 + f}{\partial \kappa / \partial P - 5/3 + (4/9) (P/\kappa)} + \frac{f}{1/3 - (4/9) (P/\kappa)} \quad (37)$$

where

$$f = (4/9) [1/\kappa - (P/\kappa^2) (\partial\kappa/\partial P)]. \quad (38)$$

The pressure dependence of Q_j is obtained by integrating the quantity

$$q_j \equiv d(\ln Q_j)/dP = j \cdot d(\ln \gamma)/dP - d(\ln N_1)/dP, \quad (39)$$

Eqs. (36)–(38) having to be substituted in Eq. (39). So far, no special equation of state has been used in this paragraph. The formulations used up to now are based on the presumption that the equation of state permits to write κ as a function of P explicitly so that the integration can be performed. This implies that $x = x(P)$ can be analytically formed from $P = P(x)$, with $x = V/V_0$. This is possible for the equations of state obtained by TAIT (see MACDONALD [31]), by MAO [33] and by GROVER et al. [16], but not for Eq. (23) by ULLMANN and PAN'KOV [47] and its special case, the equation of state by BIRCH [3]. However, since we consider Eq. (23) to be well substantiated by a comparison with measured data (ULLMANN and PAN'KOV [47]; WALZER et al. [52]), we shall make a detour so as not to be forced to introduce neglects: We regard the auxiliary quantity q_j exclusively as a function of x by eliminating P , κ , $\partial\kappa/\partial P$ and $\partial^2\kappa/\partial P^2$ on the right-hand side of Eq. (39), taking into account that for all equations of state

$$\partial\kappa/\partial P = -x\kappa'/\kappa \quad (40)$$

and

$$\partial^2\kappa/\partial P^2 = \{\kappa'' + \kappa' [(1/x) - (\kappa'/\kappa)]\}/(\kappa/x)^2 \quad (41)$$

with $x' \equiv \partial\kappa/\partial x$ and $\kappa'' = \partial^2\kappa/\partial x^2$. In the development

$$\partial P/\partial x = -\kappa/x \quad (42)$$

and $\partial^2 P/\partial x^2 = -x^{-1} \partial\kappa/\partial x + x^{-2}\kappa$ have been used. Only now do we use the special equation of state (23) for computing κ , $\partial\kappa/\partial P$ and $\partial^2\kappa/\partial P^2$ by means of Eqs. (42), (40) and (41). Now the q_j for any x in the interval $1 \geq x > 0$ can be analytically and numerically computed. x and P have a one-to-one correspondence, which is defined by Eq. (23). This makes it possible to determine Q_j as a function of P through numerical integration.

5. Results: $Q_0(P)$ — a new tool for determining the melting temperature in the Earth's core

We not only want to investigate the pressure dependence of Q_0 but also examine whether the $Q_0(P)$ of the chemical elements, when arranged according to the periodic table, exhibit a systematic structure. Only then do we want to investigate the chemical compounds. A computer was used to calculate the $Q_0(P)$ and $Q_1(P)$. At first, however, we shall discuss Q_0 . For elements, the substance constants required for computation are listed in Table 1. In Figs. 4–6, the dimensionless quantity Q_0 is shown as a function of pressure. For nearly all elements, this quantity is only slightly variable at the pressures prevailing in the core, while the quantities varying with pressure, which quantities play a role in the formation of Q_0 , i.e., T_m , κ and ρ , exhibit a significantly greater relative change in the region of the core. The $Q_0 - P$ curves of the elements show a considerable convergence. If the consideration is confined to elements which were present for the determination of the employed substance constants in the form of the densest packing, i.e., in fcc or hcp structure, the curves occur nearly exclusively in the bunches. It can be seen in Fig. 6 that the curves of the elements of the sixth period form *two* bunches in the core region. All elements of the lower bunch, except Bi, have fcc or hcp structure, the bcc structure prevails in the upper bunch. In Figs. 7, 8 and 9, the Q_0 values are shown for vanishing pressure, for the

Table 1

Physical substance constants of chemical elements used for $P = 0$. Melting temperature T_m according to Gschneidner [17], formula weight F according to Ebert [14], density ρ and bulk modulus κ for the lanthanons and actinons according to Kittel [24], density, bulk modulus and its derivative with respect to pressure for the other elements according to Ullmann and Pan'kov [47]. A significant part of the data collection in the latter paper stems from O. L. Anderson [2] and Guinan and Steinberg [18]. N_1 is the dimensionless quantity for $P = 0$ defined by Eq. (32), where $R_0 = 8.314,41$ J/(K · mol). The value denoted by a) actually applied to bcc iron, if the hypothetical melting point curve for hcp iron by Liu [29] is drawn for low pressures, one attains the same value

Element	T_m [K]	ρ [g/cm ³]	κ_0 [kbar]	F [kg/mol]	N_1	κ_1
Li	454	0.534	115	6.94	39.59	3.56
Be	1,557	1.84	1,100	9.01	41.61	4.6
B	2,498	2.31	1,785	10.81	40.22	3.26
Na	370.8	0.970	61.8	22.99	47.51	3.59
Mg	923	1.74	344.2	24.31	62.66	4.16
Al	933.2	2.697	729.1	26.98	94.00	4.7
Si	1,685	2.33	970.8	28.09	83.54	4.16
P(r)	868	2.35	192	30.97	35.06	6.68
K	336.6	0.86	31.2	39.10	50.69	3.85
Ca	1,112	1.53	163	40.08	46.18	2.7
Sc	1,812	2.98	546	44.96	54.68	2.1
Ti	1,941	4.50	1,060	47.90	69.91	4.37
V	2,178	6.09	1,537	50.94	70.99	3.5
Cr	2,148	7.194	1,600	52.00	64.76	4.89
Mn	1,517	7.47	597	54.94	34.81	5.0
Fe(ϵ)	1,808 ^{a)}	8.36	2,060	55.85	91.55	4.0
Co	1,765	8.79	1,860	58.93	84.98	4.26
Ni	1,726	8.90	1,790	58.71	82.28	6.20
Cu	1,356	8.932	1,330	63.55	83.93	5.65
Zn	692.655	7.14	647	65.37	102.86	6.40
Ga	302.8	5.91	568	69.72	266.15	3.6
Ge	1,209	5.33	724.3	72.59	98.13	4.35
As	1,090	5.77	631	74.92	90.40	5.2
Se	490	4.81	89.7	78.96	36.14	5.8
Rb	311.8	1.53	26.2	85.47	56.46	3.39
Sr	1,045	2.58	116.1	87.62	45.38	2.1
Y	1,775	4.47	410	88.91	55.26	2.1
Zr	2,123	6.53	949	91.22	75.11	4.11
Nb	2,741	8.63	1,690	92.91	79.84	6.9
Mo	2,888	10.218	2,610	95.94	102.06	4.4
Tc	2,443			98.91		
Ru	2,553	12.44	3,030	101.07	115.97	6.61
Rh	2,233	12.42	2,820	102.91	126.87	4.50
Pd	1,825	12.04	1,880	106.4	109.49	5.35
Ag	1,234	10.50	1,015	107.87	101.63	5.53
Cd	594.18	8.65	457.9	112.40	120.44	6.77
In	429.76	7.29	392	114.82	172.78	6.0
Sn	505.06	7.28	532	118.69	206.55	6.01
Sb	903.6	6.69	411	121.75	99.56	4.9
Te	722.8	6.27	233	127.60	78.90	8.3
Cs	301.8	1.83	17.9	132.91	51.81	3.17
Ba	998	3.61	94.3	137.34	43.24	2.43
La	1,193	6.16	267	138.91	60.70	3.2
Ce	1,070	6.77	239	140.12	55.60	
Pr	1,208	6.78	306	140.10	62.95	
Nd	1,297	7.00	327	144.24	62.48	
Pm	1,308			141.91		

Table 1 (continuation)

Element	T_m [K]	ϱ [g/cm ³]	κ_0 [kbar]	F [kg/mol]	N_1	κ_1
Sm	1,345	7.54	294	150.4	52.44	
Eu	1,099	5.25	147	151.96	46.57	
Gd	1,585	7.89	383	157.25	57.92	
Tb	1,629	8.27	399	158.93	56.61	
Dy	1,680	8.53	384	162.50	52.37	
Ho	1,734	8.80	397	164.93	51.61	
Er	1,770	9.04	411	167.26	51.67	
Tm	1,818	9.32	397	168.93	47.61	
Yb	1,097	6.97	133	173.04	36.20	
Lu	1,925	9.84	411	179.97	46.97	
Hf	2,495	13.25	1,080	178.49	70.13	3.95
Ta	3,271	16.62	1,910	180.95	76.46	3.15
W	3,653	19.26	3,060	183.85	96.17	3.95
Re	3,433	21.03	3,587	186.2	111.27	5.41
Os	3,300	22.58	4,200	190.2	128.94	3.4
Ir	2,716	22.65	3,580	192.22	134.53	4.83
Pt	2,042	21.47	2,770	195.09	148.25	5.18
Au	1,336.2	19.30	1,664	196.97	152.86	6.51
Hg	234.28	14.24	282	200.59	203.92	4.6
Tl	576	11.85	337	204.37	121.37	5.1
Pb	600.576	11.34	419	207.2	153.31	5.72
Bi	544.525	9.807	332	208.98	156.26	6.06
Th	2,024	11.72	543	232.04	63.88	
U	1,404	19.05	987	238.03	105.65	

pressure at the core-mantle boundary and at the inner-core boundary, respectively, in the periodic table. The points of the elements of the fourth period are linked in the three figures through continuous lines, those of the fifth period through dashed lines and those of the sixth period through dotted lines so that the figures can easily be compared to one another. For $P = 0$ and the 4th through 6th periods, one can see that from group IA to VA the three curves are running very close to one another, and this close proximity continues for the curves of the 5th and 6th period up to group VIIIA. While the quantity Q_0 of the elements shows a wide range of values for $P = 0$, i.e., scatters considerably, it can be seen in Figs. 8 and 9 that for the high pressures of the Earth's core, of which only those of its two boundary faces are shown here, the quantities Q_0 do not scatter remarkably for most elements including iron. This is even more true when one confines oneself to metals. The Q_0 of Fe is seen to lie quite close to the mean value of the Q_0 of the metallic elements. This small scattering of the Q_0 and the aforementioned stronger convergence of the $Q_0 - P$ curves in the case of fcc and hcp structures justifies the hope that it might be possible to approximately determine the melting temperature to formula weight ratio

$$T_m(P)/F = [\bar{Q}_0(P) \cdot \kappa(P)]/[R_0 \cdot \varrho(P)] \quad (43)$$

for the Earth's core as a function of the pressure P . For this purpose, $\kappa(P)$ and $\varrho(P)$ have to be taken from a reliable model of the Earth, e.g., that by DZIEWONSKI et al. [13], for the core, \bar{Q}_0 being the mean value of the Q_0 -values of all elements with a close-packed structure for a special pressure P . If F is fixed by assuming a geochemical hypothesis, $T_m(P)$ can be determined. The implementation of this suggestion, however, has to be reserved for a later paper.

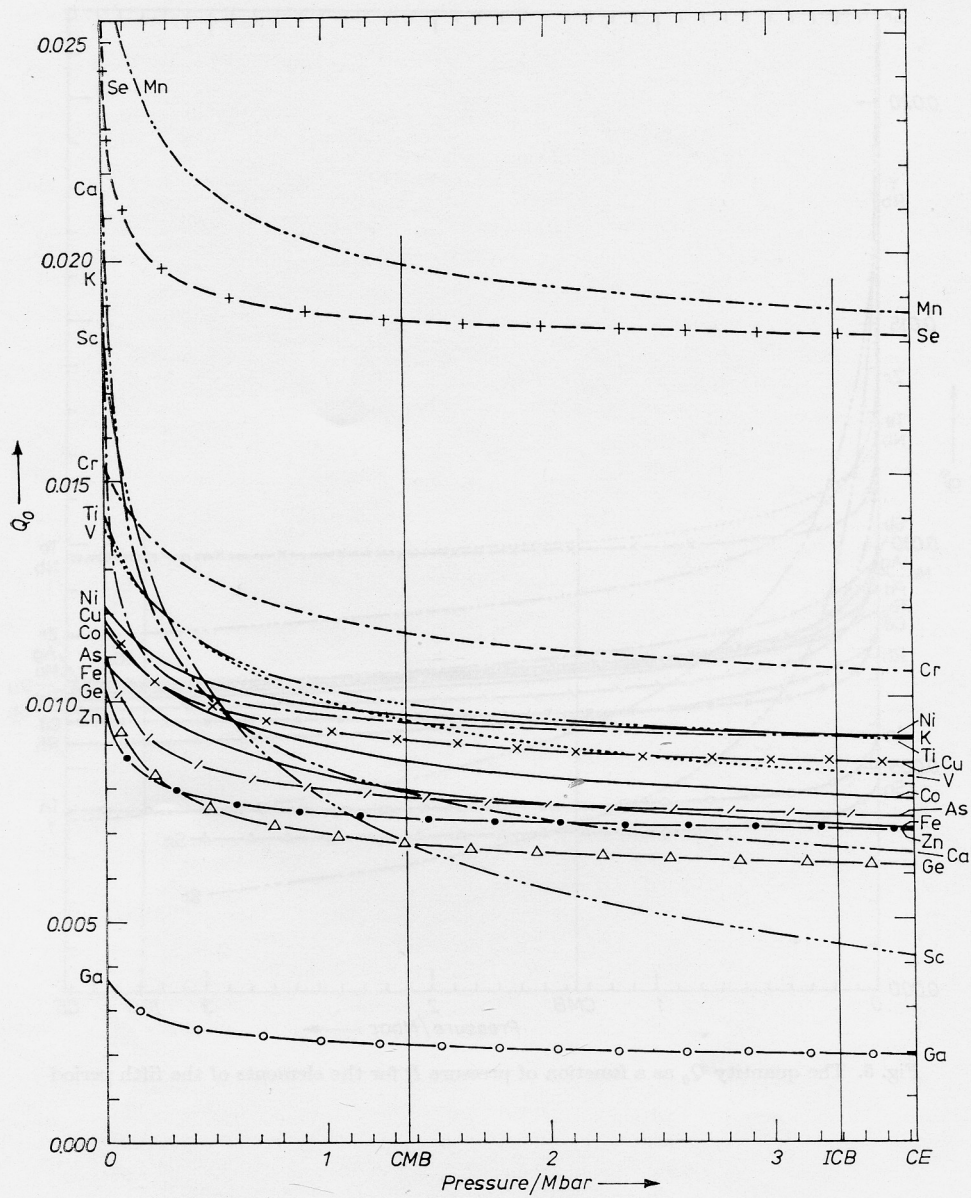


Fig. 4. The quantity Q_0 as a function of pressure P for the elements of the fourth period of the periodic table
 CMB — pressure at the core-mantle boundary, ICB — pressure at the inner-core boundary, CE — pressure in the Earth's centre. 1 Mbar = 10^{11} Pa. In Figs. 4 ··· 6, the markings of the lines for elements of the same group are identical

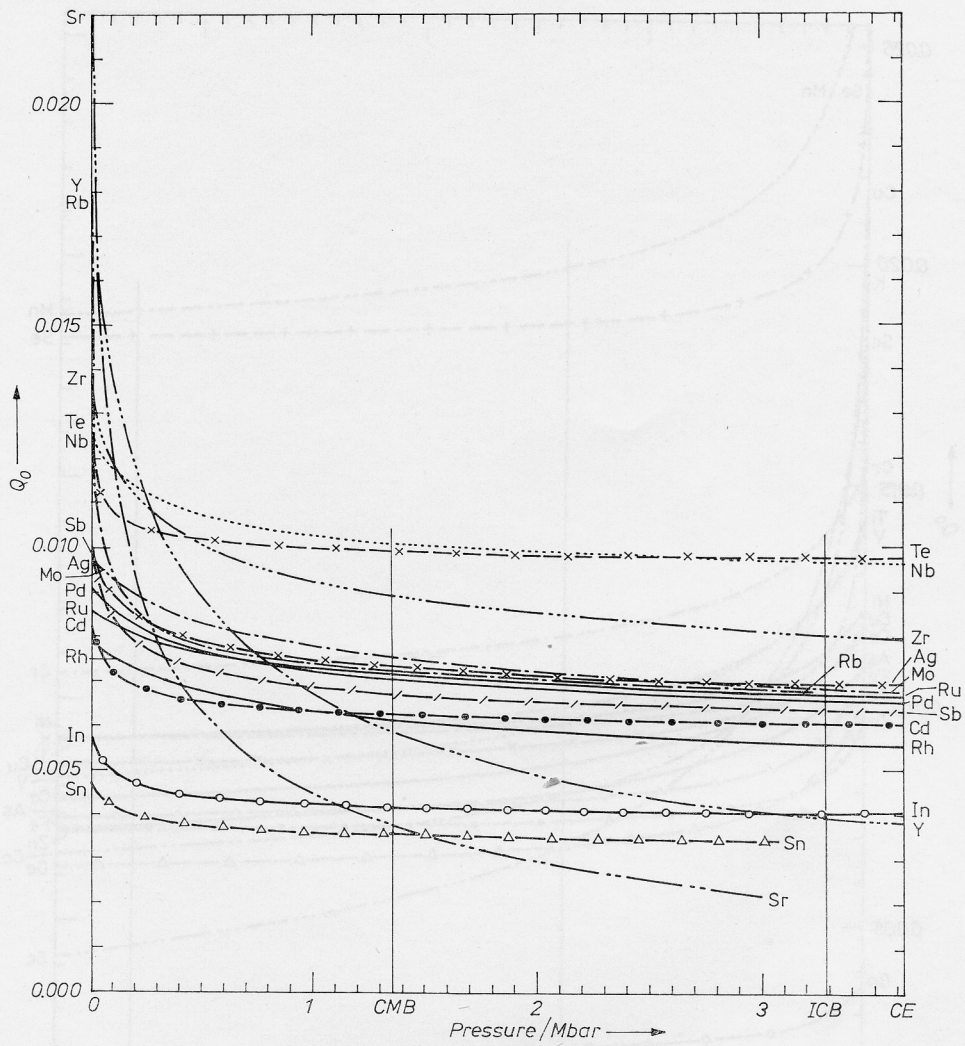


Fig. 5. The quantity Q_0 as a function of pressure P for the elements of the fifth period

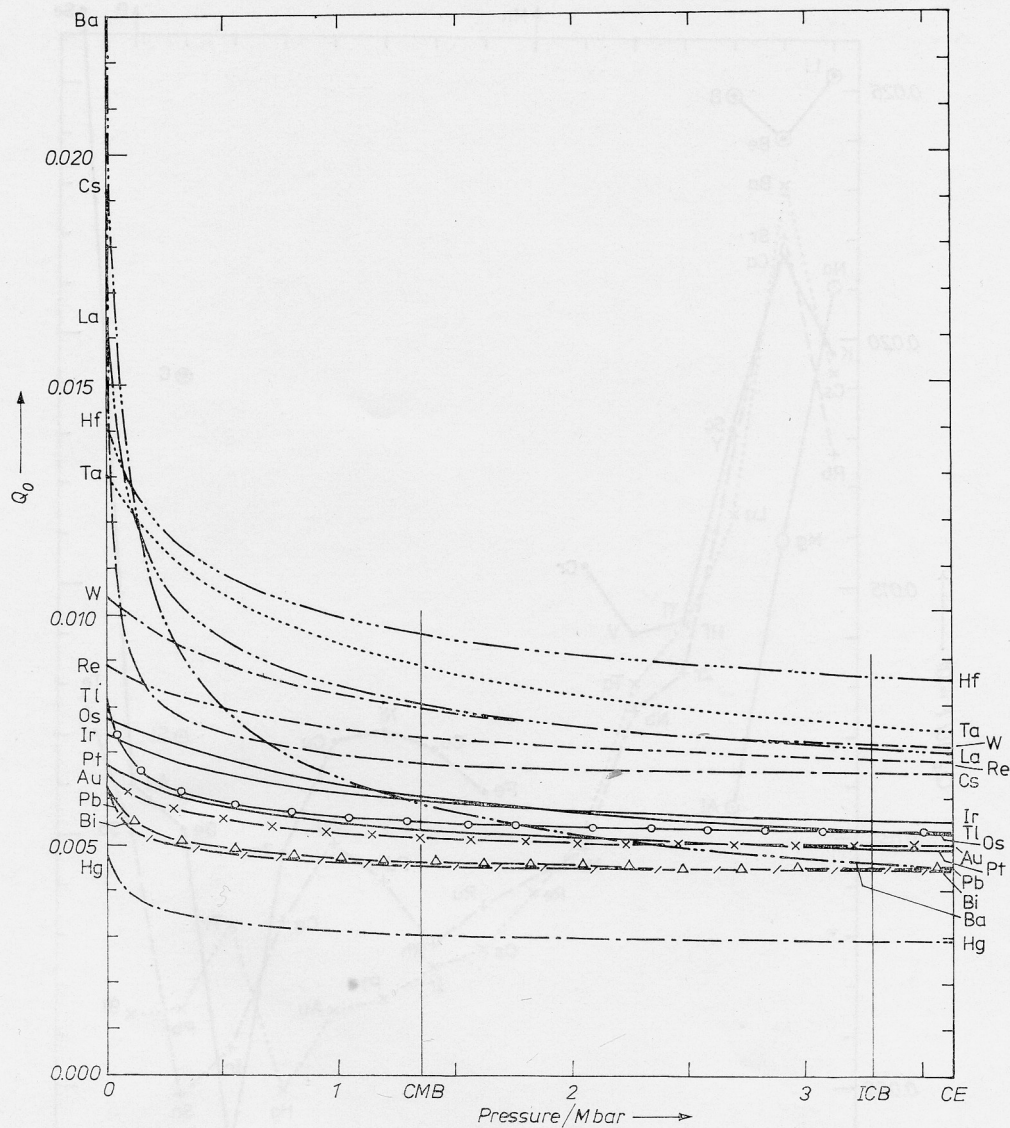


Fig. 6. The quantity Q_0 as a function of pressure P for the elements of the sixth period

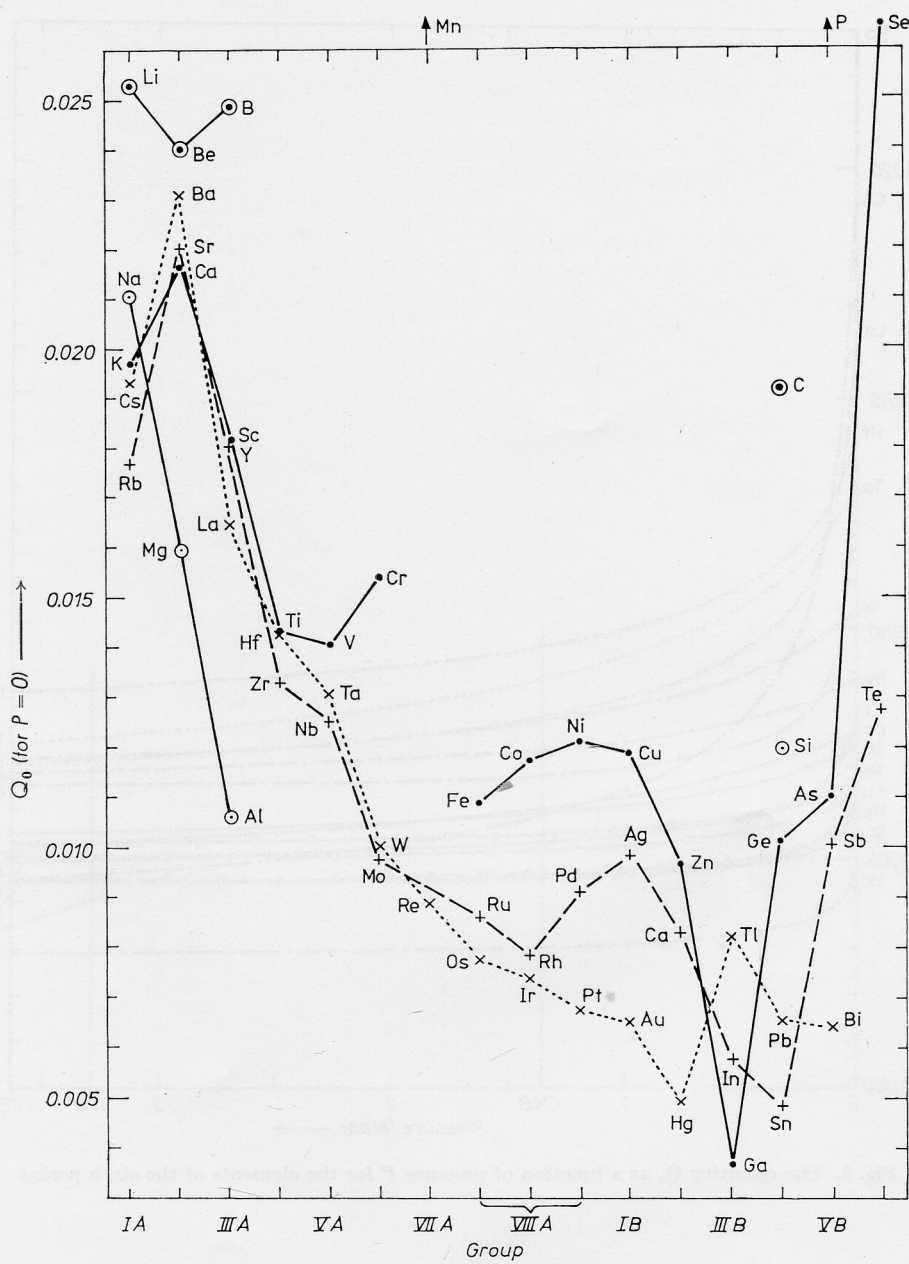


Fig. 7. The quantity Q_0 , represented in the periodic table, for vanishing pressure

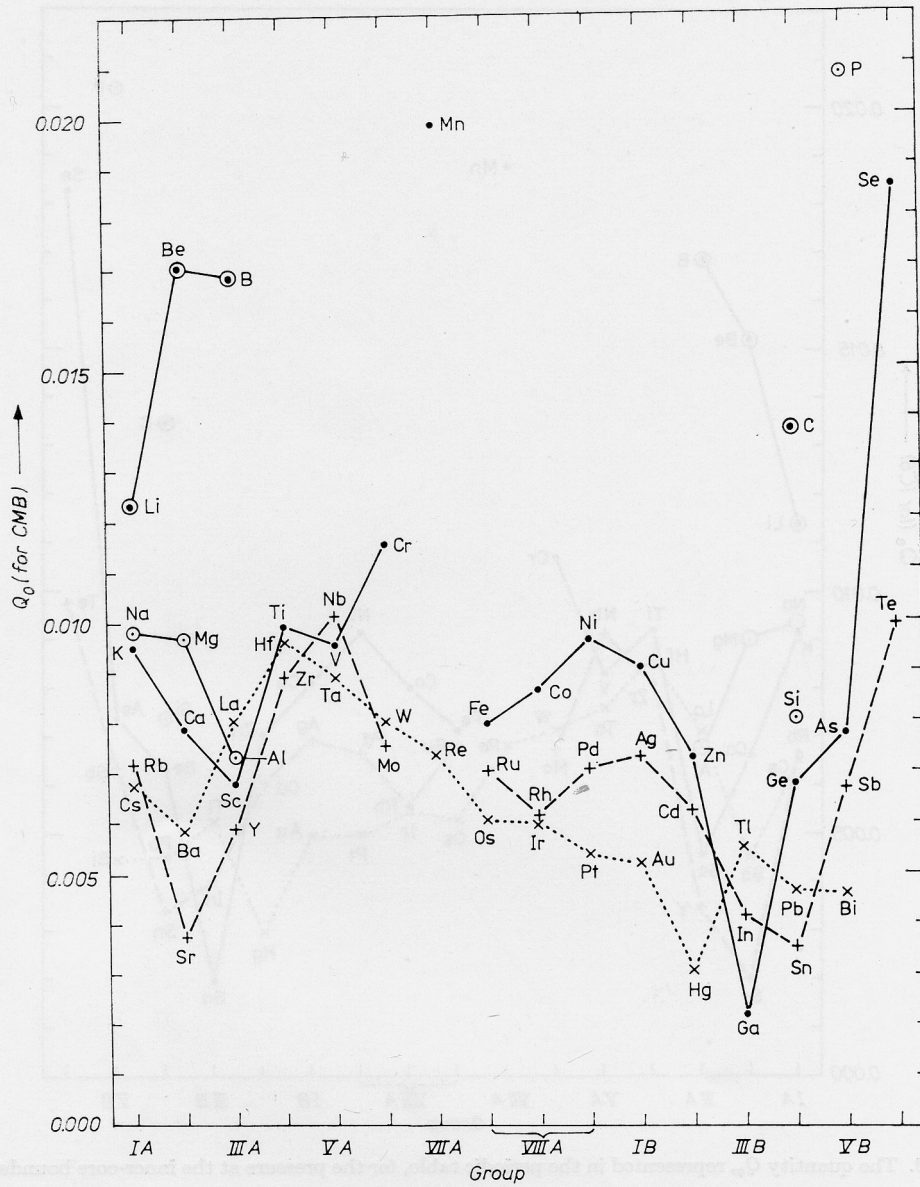


Fig. 8. The quantity Q_0 , represented in the periodic table, for the pressure at the core-mantle boundary

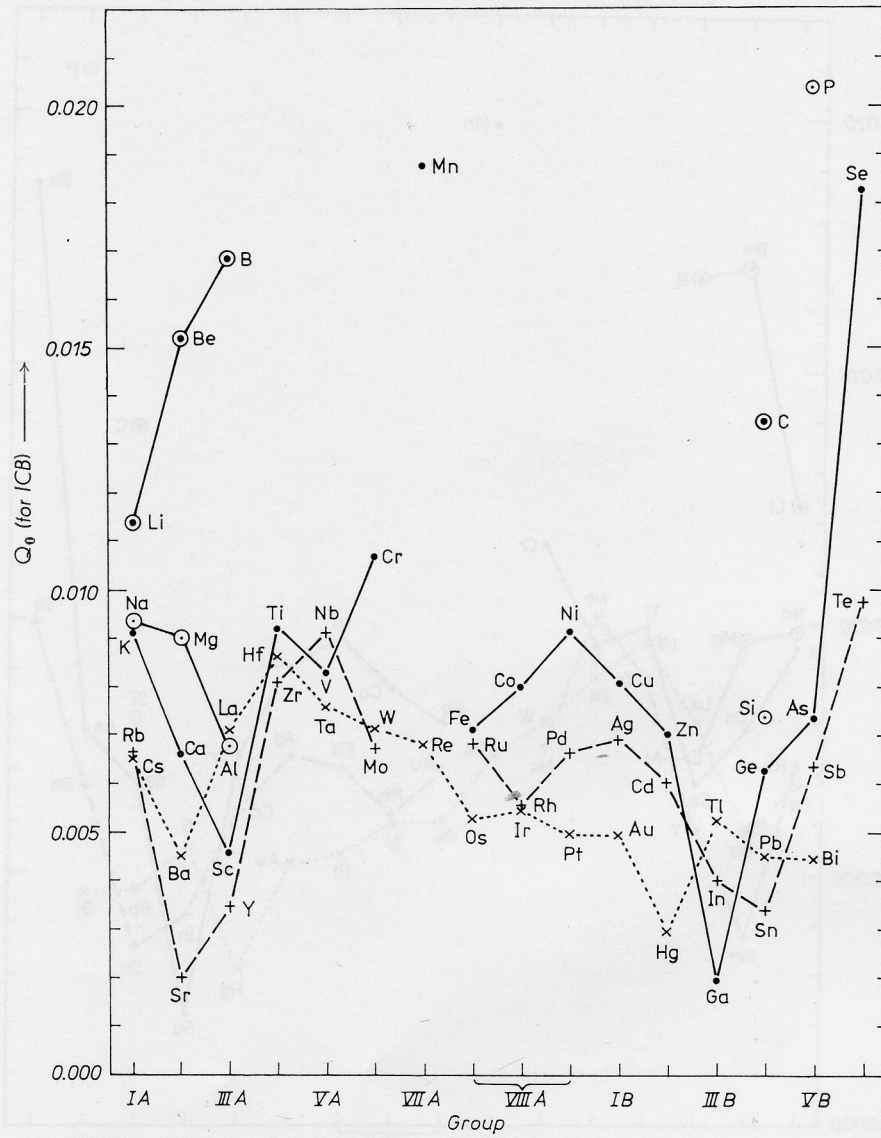


Fig. 9. The quantity Q_0 , represented in the periodic table, for the pressure at the inner-core boundary

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