To a New Conception of the Internal Constitution of the Earth

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Not all the questions occupying the minds of naturalists are equal in scope and importance. Some of them are so vast that their investigation cannot be performed by any single branch of science; they require close collaboration of various domains of human knowledge. To this category belong the questions of the origin of life, the genesis of the universe, the use of the atomic energy. Under this heading, also, comes the problem of the structure of the Earth, the solution of which inevitably requires the application of geology, physics, chemistry and seismology. Such coordination has actually been attempted in most cases by the numerous scientists, whose work is so well known that we shall refrain from citing all of them at the beginning of this short article, referring only to those, whose work is directly related to the subject under discussion.

Following this synthetic approach, we should like to attempt to outline here those concepts which best correspond to essentially diverse scientific methods, such as modern electronic chemistry, quantum mechanics, thermodynamics of high pressure, as well as seismology, with special reference to the application of this last branch of knowledge to the geological sciences. This was the course followed by V. M. GOLDSCHMIDT, for instance; but since then many new achievements have appeared in science, which do not agree with his ideas.

The partial defects of this method may be accepted if it enables us to get to a definite conclusion on the basic and decisive directives. This makes it possible to arrive at a conception of the Earth's constitution which, while partly including the existing viewpoints, is apparently new on the whole and may therefore deserve the reader's attention.

1. The Thermodynamics of Ultrahigh Pressures

Conclusions of thermodynamics do not always lend themselves to descriptive representation but have the advantage of great generality. In addition to the classical 1st and 2nd laws, a 3rd law has been introduced into it, often called the 'heat theorem' (NERNST),

which makes it possible to foresee the properties of crystals near the absolute zero (LEWIS and GIBSON). This law has both its protagonists for instance, SIMON[1] and antagonists for instance, FOWLER and STERN[2].

Much less well developed is the thermodynamic prognostication with regard to the properties of bodies under high pressures, which have been carefully examined experimentally by BRIDGMAN[3]. Among the attempts to fill this gap, we shall mention the work of LEWIS[4]. We shall also briefly outline below the results of our investigations[5] referred to in this article.

Classical thermodynamics restricts itself to noting the equality between the change of entropy (S) with volume (v) and the change of pressure (p) with temperature (T):

$$\left(\frac{\partial S}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \tag{1}$$

If we wish to go further, since here, as in the case with the 1st and 2nd laws, reference to experiment is inevitable and it shows that pure condensed bodies, when heated, expand, i.e. if the temperature is raised and the volume remains unchanged, the pressure must grow. But if $(\partial p/\partial T)v > 0$, then it follows from (1) that $(\partial S/\partial v)T > 0$, hence compression on entropy is equivalent to the influence of cooling.

Thus, with an increase in pressure we approach a condition under which

$$\Delta S = 0 \tag{2}$$

This is possible only when the entropies of all bodies approaches one and the same constant value. This value, according to the statistical considerations figured in the formulation of the 3rd law by PLANCK[6], should be taken as zero. Hence, for pure crystals, compressed to zero volume (covolume), the entropy tends to become zero:

$$S = 0 \lim v \to 0 \tag{3}$$

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[1] F. SIMON, Ergebnisse der exakten Naturwissenschaften, vol. 9 (1930), p. 222.
[2] R. FOWLER and S. STERN, Rev. Mod. Phys. 4, 637 (1932).
[3] P. BRIDGMAN, Phys. Rev. 2, 57 (1940); The Physics of High Pressure (London 1949).
[4] G. N. LEWIS, Zeit. physik. Chem. Festschrift, p. 532 (1927).
[5] A. F. KAPUSTINSKY, Doklady Acad. Scien. USSR (russ) 18, N 4, 280 (1945).
[6] M. PLANCK, Treatise on Thermodynamics (New York 1945).

We do not refer here to other various formulations of this proposition, which could be termed the 4th law of thermodynamics. All of them are to a great extent postulative, since there are no direct proofs and much still remains subject to dispute. Thus, it is generally uncertain whether a crystalline state of matter is possible under ultrahigh pressures, and, therefore, whether our postulates are satisfactory as applying to critically compressed crystals. Possibly the Earth's core is in a quasi-crystalline state, partly similar to that of ordinary water. Excessive scepticism would in any case be unwarranted. True, high temperatures also change the properties of matter, and yet we can successfully apply the third law to any temperature range, as in astrophysics, for instance, where we treat the conditions investigated as critical.
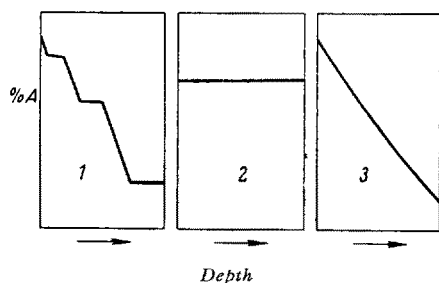

Depth

Fig. 1.—Change of chemical composition of the Earth with depth.

Applying the above generalizations to the examination of the nature of the interior parts of our planet, we may observe first of all that the division of the Earth into four chemically distinct zones, as suggested by V. M. GOLDSCHMIDT as early as 1927 and accepted by many geochemists, is now often questioned. To the usual arguments, the fact may be added that GOLDSCHMIDT[7] based his theory upon the presumption of the immutability of the ordinary properties of matter, while their radical change with ultrahigh pressures is now no longer subject to any doubt (see next paragraph).

Equally unplausible seems the diametrically opposed point of view, recently set forward by LODOCHNIKOV[8], that the Earth as a whole constitutes a chemical homogeneity, since it is impossible to regard as totally precluded a certain growth of concentration of heavy particles from the crust to the centre under the effect of the gravitational forces acting over a long period of time. The change of the Earth's composition with depth is subject, on the whole, to the law of continuity. This difference of opinion may best be represented graphically (see Fig. 1) by plotting the depth on the X-axis and the content of some relatively light element on the Y-axis (% A). Then GOLDSCHMIDT's theory will correspond to a stepped curve (1), LODOCHNIKOV's one to a horizontal line (2), and our views to a smoothly dropping curve (3).

Hitherto we have assumed homogeneity as characterizing the Earth's composition. Such is not the case with the physicochemical properties. Seismology (which permits more subtle distinctions to be observed) roughly but unmistakably indicates the existence of a special kernel at a depth of 2900 km. According to what we have said in the present chapter, irrespective of the real thermal state, the properties of crystals under rising pressure increasingly approach the properties characteristic of condensed matter at absolute zero temperature. But inasmuch as pressures in the order of a million atmospheres practically approach infinitely high pressures, it may naturally be taken that, beginning with the border of the central kernel and further down, the entropy, thermal capacity, compressibility and thermic expansion of crystals reach zero, while the heats of transformation become equal to free energies. In other words, the Earth's central zone, no matter what its temperature, represents a body requiring a negligible amount of heat to become heated, a body approximating in its physical properties (as will be shown in the paragraphs below) to a metallic state (possessing, inter alia, high conductivity), a body whose energy is in a 'juvenile' non-degenerate state, since its entropy is practically equal to zero. The central zone or kernel is a region of bodies with zero entropy.

Energy degeneration begins only beyond its boundaries, and increases when approaching the periphery.

2. Thermal State of Earth

It is generally held that temperature, like pressure, grows with depth, reaching some 5000°C at the Earth's centre. This fully harmonizes with the Kant-Laplace theory, which depicts the Earth as a body with a steadily diminishing temperature. This theory, however, has already lost its former significance and has begun to give way to others, for instance, to those in which it is supposed that only the shells are heated while the centre remains cold.

The data of radiochemistry has proved of special importance in showing that the heat generated by radioactive transformations is sufficient to maintain the high temperature of the planet as a whole. Computations made first by KHLOPIN[9] and later by LATIMER[10], proved convincingly that the number of radioactive atoms contained in the Earth absolutely suffices to heat it to a temperature of some thousands of degrees. But inasmuch as the number of such atoms first in-

[7] V. M. GOLDSCHMIDT, *Geochemistry* (London 1954).

[8] V. N. LODOCHNIKOFF, Zapiski Wsesojusn. Mineral Ob-wa (russ), *58*, 207, 428 (1939).

[9] V. G. KHLOPIN, Izvestia Acad. Sciences of USSR Geogr. and Geophysics (russ) N 2 (1937).

[10] W. LATIMER, Science *112*, 101 (1950).

creases and then decreases with depth, VERNADSKY[11] expressed the conjecture that the temperature first rises and then falls so that the kernel forms a comparatively cold part of the planet.

Such an explanation would be plausible had not the thermal capacity of the substances composing the globe changed with pressure, hence also with depth. Since the temperature T, the amount of heat generated by radioactive decay Q, and the thermal capacity C are interconnected by the usual equation

$$T = \frac{Q}{C} \qquad (4)$$

with $C = $ const., T must change in the same way as Q, and the above may be expressed by the upper part of Figure 2, I. But, as already indicated earlier, thermal capacity with the approach to the centre diminishes to values approaching zero, which is graphically expressed by the middle part of Figure 2, II. A combination of I and II produces the resultant lower part of the Figure 2, III, according to which in a stationary
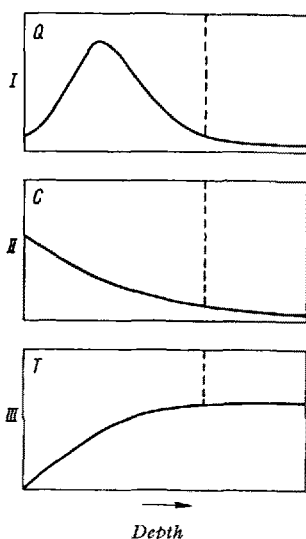

Fig. 2.—Comparison: (a) of the change in the amount of heat Q generated by the decay of radio elements, (b) the change of heat capacities C, and, finally (c) the temperature T, from the periphery to the centre of the Earth.

state the negligible amounts of heat generated by radioactive substances are sufficient, in view of the infinitely small thermal capacity, to maintain the temperature at the high level already reached. This level corresponds to the temperature of that part of the Earth where such small thermal capacities are reached, i.e. the beginning of the kernel zone. It amounts to 2000–2500°C. And since, as we have already stated, the kernel must possess high heat conductivity too, its temperature at all points can be only one and the same.

Thus, our theory, advanced in accordance with the data of radiogeology and radiochemistry, permits the

[11] V. I. VERNADSKY, Trudy XVII International Geolog. Congress (russ) 1, 215 (1939).

central kernel of the Earth, beginning with the depth of 2900 km, to be regarded as an isothermic hot zone with a temperature of approximately 2000–2500°C.
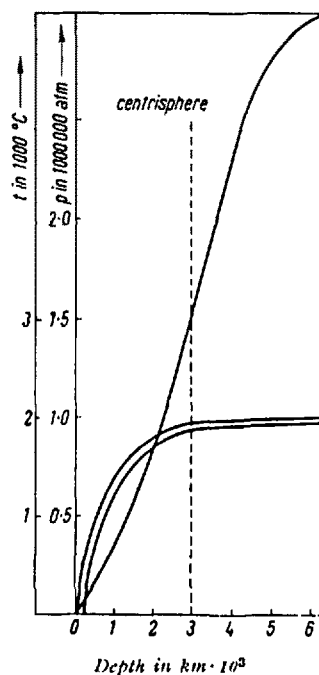

Depth in km· 10^3

Fig. 3.—The changes in pressure and temperature (double line) with depth. The vertical dotted line denotes the border of the central zone of the Earth.

Figure 3 graphically shows how the growth of pressure and the growth of temperature differ with the depth of penetration into the interior of the Earth.

3. Electronic Isomerism of the Atoms and Degeneration of the Chemical Properties

It is well known that the first 18 elements of the Mendeleev system differ from the others both geochemically and by the structure of their atoms: they constitute 92% of the Earth's crust, which testifies, perhaps, to their relative stability, and they also have the electronic structure of the atoms exactly corresponding to the filling of all the levels provided for by the Pauli exclusion principle. It is also of interest to note that the nuclei of their atoms contain an equal number of protons and neutrons.

As the compression of the atoms grows, the electrons become capable of shifting to deeper energy levels, i.e. to unfilled orbits closer to the nucleus, without violating the exclusion principle. The resulting atoms of one and the same element possessing an identical composition, i.e. the same number of electrons, protons and neutrons, will differ, however, from the original atoms by their structure, hence also by their properties. We shall name this phenomenon 'electronic isomerism of atoms'.

Table I. Electronic Isomerism of Calcium Atoms

Quantum level		1 s	2 s	2 p	3 s	3 p	3 d	4 s
Distribution of electrons	in calcium atom	2	2	6	2	6	—	2
	in isocalcium atom	2	2	6	2	6	2	—

An illustration may be provided by the atoms of the calcium element whose atomic number is 20. Normal calcium (Ca_{20}) and 'isocalcium' (Ca_{20}) which is obtainable from the former by means of pressure, differ substantially from one another in a quantumchemical respect, inspite of·identity of composition, as Table I clearly shows.

The more complex the atoms, the more varied may the possible 'isomerism' be. The pressures required for such isomerism to develop are not too high. STERNHEIMER[12], using the Wigner-Seitz's quantum theory, has calculated the energy of transition of an electron from the 6-s level to the 5-d level. If his data (45000 atm.) are re-calculated for the depth of the Earth, we shall get about 100 km. Of course, the energies of isomerization of atoms are different for different elements, but these differences are not too great and apparently correspond to depths of between 50 and 120 km. In all probability, the 'Mochorovicic discontinuity', which is well known to geologists and seismologists, exactly corresponds at a depth of 40–60 km to the beginning of this new zone, in which the atoms of most elements begin to acquire new, anomalous and still practically unknown chemical properties. Hence, atoms with well-known chemical properties exist only in the outer shell of the Earth, which is fairly thin and stretches only to the 'Mochorovicic discontinuity'. Deeper down, these properties degenerate and although chemical reactions do take-place, in most systems the laws governing them are totally unknown, inasmuch as most chemical elements there undergo a radical change in the electronic structure of their atoms. The deeper we penetrate this zone, the more substantial are these changes and the deeper are the layers of electrons effected by them. It may be properly named a zone with 'degenerate chemical properties'.

While degeneration of energy increases from the Earth's centre to its periphery, the degeneration of chemical properties increases from the periphery to the centre.

4. Annihilation of Chemical Properties under Ultrahigh Pressures

Chemical reactions represent a regrouping of electrons in atomic, molecular and crystalline structures, possible only because of the fixed electronic 'architecture' of these particles, and its absence would correspond to the disappearance of chemism. But since Mendelcev's periodic system of electrons expresses precisely the distinctions in the electronic structure of the atoms, the question naturally arises, does the periodical nature of the properties depend upon the pressure, and if so, how? If, for instance, the periodicity becomes less and less pronounced with pressure, then we may hope to find, by extrapolation, pressures at which it does not manifest itself at all, when, therefore, 'annihilation' of chemical properties takes place, i.e. chemical transformations become impossible.
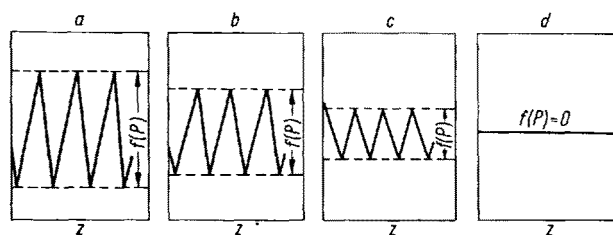

Fig. 4.—Change of the function of periodicity $f(P)$ with pressure p. In each figure (a), (b), (c) and (d) the dotted lines indicate the borders within which the properties plotted on the Y-axis vary from the atomic numbers Z. From (a) to (c) the pressure rises.

At present this problem lends itself to solution, although very roughly indeed. Yet RICHARDS[13] showed that the compressibility of simple bodies (elements) changes periodically with atomic weight. Making use of BRIDGMAN's analogous data for 30000 and 100000 atmospheres, WERESCHAGIN and LICHTER[14] demonstrated that periodicity manifests itself right up to these high pressures, its manifestation becoming less and less pronounced with the rise of pressure. This is graphically represented in Figure 4 where from left to right, from lower to higher pressures, the decrease in the range of periodic changes of a given property, depending on the atomic numbers of the elements Z, are is given.

Let us introduce into the subject the 'periodicity function' $f(P)$, which represents (see Fig. 4, arrow to the right) the distance between the dotted lines limiting the fluctuations observed, and provides, as it were, a relative 'startup' of the periodic changes. Obviously, the smaller the value of this function the less the periodicity manifests itself, while its reduction to zero will correspond to complete disappearance of periodicity, and chemical properties as well.

[13] T. RICHARDS, J. Amer. chem. Soc. *37*, 1643 (1915).

[14] L. WERESCHAGIN and A. LICHTER, Doklady Acad. Scien. USSR (russ) *86*, 745 (1952).

[12] R. STERNHEIMER, Phys. Rev. *78*, 235 (1950).

Table II presents this function as computed by us on the basis of the materials given in WERESCHAGIN and LICHTER's article for different pressures (which we express in the form of logarithms, lgp in view of their large scales). The same data are represented graphically in Figure 5. The points, although few, fall on a

Table II
Charge of periodicity function *f*(*P*) with pressure

Pressure p in atm	Periodicity function f(P)	Pressure logarithm log p
1	2·5	0·00
30 000	1·3	4·48
100 000	0·9	5·00
(1 400 000)	0·0	(6·15)

cally in Figure 5. The points, although few, fall on a smooth curve which crosses the zero value of the periodicity function at pressures approaching 1 400 000 atmospheres (log p = 6·15).
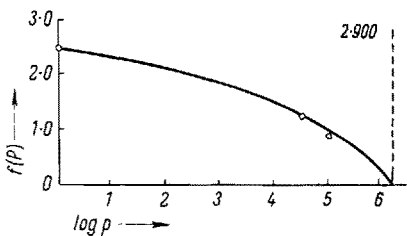

Fig. 5.—Change of function of periodicity, computed from the compressibility of the chemical elements, with pressure (more exactly, with the pressure logarithm plotted on the X-axis). The dotted line denotes the border of the central kernel.

Rough as this extrapolation may be, the above data reveal an interesting connection between geochemistry and seismology. Indeed, the pressure obtained by such extrapolation corresponds to a depth of 2900 km, i.e. the very depth to which all seismic data agree as constituting the beginning of the Earth's central zone.

At present we are in possession only of one periodically changing property, which has been studied for many elements and for such high pressures, viz., compressibility. There is no ground to assume, however, that for the other properties the picture would differ substantially. All this permits the Earth's central zone to be regarded as a geosphere in which no chemical reactions can take place. Its specific and most characteristic feature is, apparently, not its chemical composition, since the chemical properties are obviously erased here, but the electronic state of matter. Inasmuch as the chemical properties in it are 'annihilated', it may naturally be named 'a zone of zero chemistry'.

5. 'Metallization' of the Earth's Interior

The progress of quantum mechanics has given rise to various interesting explanations of the processes occuring within the stars and planets. According to

WIGNER and HUNTINGTON[15], a quantum-mechanical calculation of the compressibility of an elementary hydrogen lattice, reveals the possibility of the appearance of free electrons characteristic of a metallic condition, under the action of sufficient pressure. KUHN and RITTMANN[16] suggested the existence of a hydrogen kernel in the Earth's centre and believe a *partial* removal of hydrogen from the earth as a whole to be definitely possible, while KRONIG, DE BOER and KORRINGA[17] indicated the possibility of hydrogen changing to a metallic state with a density of 0·8 g/cm^3 under a pressure of 700 000 atm. RAMSEY[18], in a series of works, discussed in detail the possibility of a transition of bodies into a metallic state, and of a radical change of their physical properties under high pressure in the interior of stars and planets. A review of these researches, as well as the dynamic conception of the Earth's internal structure, have recently been given by EGYED[19]. To this may be added that, from 1936 the author of this paper has also published a number of works (in Russian) to substantiate the idea that inside the Earth the condition of bodies in many respects resembles that observed near the absolute-zero temperature, any body changing to a metallic state under sufficiently high pressure[20].

It follows from the considerations given in the previous sections that this conception may well be argued and satisfactorily agrees with a number of works by other authors.

Indeed, according to quantum chemistry, under sufficient pressure the destruction of the electronic shells of the atoms is inevitable, so that the Earth's kernel, whatever its 'composition' may be, must be in a 'metallized' state, i.e. the nuclei of the atoms immersed in plasma are in a tightly packed state. According to the thermodynamics of high pressure, this homogeneous isothermic phase with a temperature of about 2000–2500°C has the properties of a system located, as it were, close to the absolute-zero temperature. Its entropy, heat capacity, compressibility approach zero, while its electric and heat conductivity sharply increase; it is even possible that the phase is in a state of supra-conductivity and suprafluidity.

We arrive at this conclusion by theoretical analysis, but it may be added that recent experiental investigations have confirmed these ideas.

[15] E. WIGNER and H. HUNTINGTON, J. chem. Phys. *3*, 764 (1935).

[16] W. KUHN und A. RITTMANN, Geol. Rundschau, *32*, 215 (1941). – W. KUHN, Naturwiss. *30*, 689 (1942); Exper. *2*, 391 (1946); Naturwiss. *33*, 311 (1946). – W. KUHN und S. VIELHAUER, Geochim. cosmochim. Acta *3*, 169 (1953).

[17] R. KRONIG, J. DE BOER, and J. KORRINGA, Physica *12*, 245 (1946).

[18] W. RAMSEY, Monthly Notices Royal Astronom. Soc. *108*, 406 (1948); Geophys Supplement 5, N 9 (1949).

[19] L. EGYED, Geol. Rundschau *46*, 101 (1957).

[20] First short communication see A. KAPUSTINSKY, Sbornik akad. Vernadskomu k 50-letiy deyatelnosti, *1*, Acad. Scienc. USSR 1936 (russ). Last one see: Sbornik Voprosy geoch. i. mineralogii. Acad. Scienc. USSR, 1956 (russ). – See also A. KAPUSTINSKY, Nature *180*, 1245 (1957).

Thus, ALDER and CHRISTIAN[21], by measuring the electric conductivity of highly compressed mineral crystals, demonstrated that under high pressures these bodies acquire the same degree of electric conductivity as metals.

Since in the phase considered all electrons are free and collectivized (and the most characterstic feature of the metallic state is the presence of free electrons belonging to the lattice as a whole), any chemical reactions are impossible here. The kernel or region of 'squashed' atoms, as pointed out above, represents a zone of 'zero chemistry'. Here both oxygen and silicium are as much metals as iron and sodium. Formally, by their atomic numbers, various elements may be represented here. But the usual meaning of the term 'element' is completely lost here since we are dealing generally with a universally 'metallized' phase. By its properties it must closely approach the ironnickel kernel which was considered by earlier theories of geochemistry, with those important specific differences of principle which were dealt with above.

6. Geospheres and General Conclusions Concerning their Physio-Chemical Properties

As a result, we come to the conclusion of the existence of three geospheres – peripheric, intermediate and central – a classification which can be given in terms of both geology and chemistry:

Classification of Geospheres

Geological	General	Chemical
Crust or lithosphere Intermediate eclogitic shell «Metallized» kernel of Earth	Perisphere (50–120 km) Intersphere (120–2900 km) Centrisphere (2900–6370 km)	Normal chemistry zone Degenerated chemistry zone Zero chemistry zone

To this should be added, of course, the three surface geospheres, the atmosphere, hydrosphere and biosphere, which have not been discussed above, because they have relatively smaller dimensions and mass.

All known chemical reactions, subject to the classical laws of chemistry, occur mostly on the periphery of the Earth in the perisphere, which represents a heterogeneous, i.e. multiphased and comparatively thin, shell with more blurred and less distinct borders than the kernel border.

The intermediate zone, the 'intersphere', which is mainly composed of eclogitic rocks, is characterized by the emergence of phasial homogenization and passing of the atomic electrone to deeper and unfilled energy levels under the action of higher pressures. The chemical properties of substances increasingly 'degenerate',

more and more diverse types of electronic isomerism and far-reaching ionization of atoms develop, and the processes begin to follow laws as yet unknown to us, about which we are able to form only a general idea.

The centrisphere is completely devoid of any chemical properties. The electronic shells are subject to destruction, and no reactions can be achieved. This is a zone of 'zero chemistry', a zone of a homogeneous phase, consisting of atomic nuclei immersed in plasma, common to all nuclei and possessing the properties of the metallic state. This uniform alloy appears to be a quasi-crystalline fluid in some respects similar to water, according to the well known theory of Bernall and Fowler. Here all bodies found in nature – quartz, olivines, carbides, etc. – regardless of their chemical origin, are transformed into a structurally homogeneous 'nuclear metal', 'metallization' occurs under pressure. The high heat conductivity of such a phase makes the existence of a temperature gradient in it impossible, and that is why the central kernel constitutes an isothermic phase. The main sources of heat, maintaining a more or less stationary condition of the Earth, are the processes of radiochemical transformations of the Earth as a whole, sufficient to maintain the centrisphere temperature at about 2000–2500°C. Despite such a high temperature, the bodies constituting the centrisphere behave, as a result of the action of ultrahigh pressure, as if they were in temperatures approaching absolute zero.

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There is no doubt that the geochemical theory of the laminated structure of the Earth is more in the nature of a hypothesis, still to be checked and proved. It is supported, however, by the fact that it is in agreement with modern chemistry, quantum mechanics and seismology.

Zusammenfassung

Auf Grund der Ergebnisse der modernen Elektronenchemie, der Quantenmechanik, der Ultra-Hochdruck-Thermodynamik und bis zu einem gewissen Grade der Seismologie wird eine neue Ansicht über die Struktur der Erde postuliert. Das Modell einer Kugel, die stufenweise mit Zunahme der Tiefe ihre Zusammensetzung ändert, erscheint wahrscheinlich. Die von den Seismologen beobachtete Zonierung beruht nicht auf drastischen Veränderungen der Zusammensetzung, sondern auf einer stetigen Degeneration der chemischen Eigenschaften der Atome, die durch einen Umbau der atomaren Elektronenstruktur unter Einwirkung von Hochdruck zustande kommt. Die äussere Hülle, «Perisphäre» (50–100 km), umfasst eine Zone wohlbekannter chemischer Struktur. Auf sie folgt die «Intersphäre» (bis 2900 km), die eine radikale Änderung der Eigenschaften der Atome aufweist, beruhend auf einem Übergang der Elektronen auf ein tieferes Energieniveau, das heisst «Degeneration» der chemischen Eigenschaften. Im Innersten befindet sich der Kern, «Zentrisphäre», eine «metallisierte» Phase mit einer konstanten Temperatur von 2000–2500°C, deren chemische Eigenschaften O sind und in der die Kerne in ein elektronisches Plasma eingebettet sind.

[21] B. ALDER and R. CHRISTIAN, Phys. Rev. *104*, N 22 (1956).