PHASE TRANSITIONS AND CRITICAL PHENOMENA IN THE EARTH’ S ENVELOPE

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Abstract

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In recent years a large body of factual material has been accumulated on phase transformations having the character of continuous phase or critical transitions. These transformations undoubtedly play a major role in the processes of development of the Earth and other planets, where enormous pressures and elevated temperatures favor the transition of matter into critical and supercritical states.

It may be regarded as established that the Earth' s mantle, in its chemical composition, is rather close to the average composition of the silicate phase of stony meteorites. At the same time, experiments on the zonal melting of chondrites, carried out at the Institute of Geochemistry and Analytical Chemistry of the Academy of Sciences of the USSR, showed that at a temperature of 1800-2000° C all the substance of chondrites is completely volatilized ([1]). These data make it possible to conclude that the temperatures prevailing in the interior of the heated parts of the envelope possibly exceed the temperatures of elasticity of rock vapors at normal pressure.

According to Jeffreys, the rocks composing the Earth' s mantle are in the solid state, since in the Earth's envelope down to the boundary with the core there are no regions that do not transmit transverse elastic oscillations. However, since the material of the mantle is heated to a high temperature, phase transformations may arise in the Earth' s envelope; analysis of these from the standpoint of thermodynamics is of great importance for understanding the physical processes that occur in the planet' s interior.

Let us recall that usually the critical point is determined by two equations connected with the p—v diagram,

$$(\partial p/\partial v)_T = 0, \tag{1}$$

$$(\partial^2 p/\partial v^2)_T = 0. \tag{2}$$

However, equation (1) determines not a point but a curve, the so-called spinodal. Every system is thermodynamically stable only under the condition $(\partial p/\partial v)_T < 0$ and unstable if $(\partial p/\partial v)_T > 0$. Therefore $(\partial p/\partial v)_T$ is called the coefficient of stability. The line $(\partial p/\partial v)_T = 0$, separating the region of stable states from the region of unstable states (the spinodal), is the boundary of stability. Hence it follows that the condition $(\partial p/\partial v)_T = 0$ is not characteristic of the critical point. The second condition $(\partial^2 p/\partial v^2)_T = 0$ is also fulfilled not only at the critical point. Therefore the critical point is determined by the simultaneous fulfillment of both conditions. The line at whose points only one of the two conditions characterizing the critical point, $(\partial^2 p/\partial v^2)_T = 0$, is satisfied has been called the quasispinodal.

Equations (1) and (2) show that at the critical point the reciprocal values of the derivatives $(\partial p/\partial v)_T$, i.e. $(\partial v/\partial p)_T$, pass through an extremum equal to infinity and, furthermore, that on the curve p—v or v—p there is a point of inflection. It can be shown that the points of the quasispinodal correspond to extrema of the first derivatives, minima for $(\partial p/\partial v)_T$ and thereby maxima for the reciprocal quantities $(\partial v/\partial p)_T$.

Indeed, the minimum of $(\partial p/\partial v)_T$ is determined by the equation

$$\frac{\partial}{\partial v}(\partial p/\partial v) = 0 \tag{3}$$

and by the inequality

$$\frac{\partial^2}{\partial v^2}\left(\frac{\partial p}{\partial v}\right) > 0. \tag{4}$$

But (3) determines on the primary p-v curve an inflection point, coinciding with condition (2), which determines the critical point; however, this point does not lie on the spinodal

$$(\partial p/\partial v)_T = 0,$$

and therefore there is every reason to call it a point of the quasispinodal.

The line of phase equilibrium corresponds to a real phase transition, whereas the line $(\partial^2 p/\partial v^2) = 0$ corresponds only to points at which the continuous process of internal rearrangement of a substance under the action of external forces reaches its greatest development. In one respect the quasispinodal is similar to the phase-equilibrium curve. Passage through the phase-equilibrium curve is accompanied by the expenditure of heat $Q = T(S'' - S')$ (S is entropy) and work $A = p(v'' - v')$, since S and v are different for the two phases. In passing through the curve $(\partial^2 p/\partial v^2) = 0$, S and v change continuously, but the derivatives $T/c_p = (\partial T/\partial S)_p$ and $(\partial p/\partial v)$ pass through a finite extremum. Over a short interval of temperatures and pressures,

$$Q = \int_{T_1}^{T_2} c_p \, dT \quad \text{and} \quad A = \int_{v_1}^{v_2} \left(\frac{\partial p}{\partial v}\right)_T dv$$

are nonzero. Thus, crossing the line $(\partial^2 p/\partial v^2) = 0$ along an arc of finite dimensions, we effect, as it were, a continuous phase transition. The substance on one side of it has properties similar to those of a low-temperature phase (for example, a solid), and on the other side properties similar to those of a high-temperature phase (for example, a liquid or gas). Transitions of this kind —that is, phase transformations consisting in a continuous change of properties, occurring over a certain, sometimes very considerable, interval of temperatures and pressures—have proved to be very widespread. Transitions in a number of crystalline polymers have precisely the character of such transformations: the mechanical $(\partial p/\partial v)_T$ and thermal T/c_p stability coefficients pass through sharply pronounced minima. The value of $(\partial p/\partial v)_T$ then falls to a magnitude of the same order as $(\partial p/\partial v)$ for gases, which has given some investigators reason to regard these materials as substances to which the theory of gases may be applied.

In some cases the fall in stability becomes close to zero (such a case is found, for example, in the α-β transition in quartz), and the transition becomes so close to critical that the question can finally be resolved only with the aid of exceptionally precise experimental investigations.

When the boundaries of the region of reduced stability are crossed, the stability coefficients pass through minima, the most important of which are $(\partial p/\partial v)$ and T/c_p; in addition, in the region of reduced stability the properties of the substance change rapidly, but continuously, from values characteristic of the low-temperature phase to values characteristic of the high-temperature phase.

The region of reduced stability apparently has finite dimensions and ends at a supercritical point, which is the apex of the quasispinodal ([3–5]).

From the thermodynamic point of view, passage through the quasispinodal is expressed in passing through extrema of the following quantities: c_p, β_T, and

γ_p, where β_T is the compressibility, and γ_p is the coefficient of thermal expansion. Consequently, a detailed study of these quantities for different rocks over a wide range of temperatures and pressures will make it possible to answer the question of the depths inside the terrestrial sphere at which continuous phase transitions occur.

In Fig. 1, the data for which were taken from work ([6]), graphs of $\varepsilon(T)$ are presented for tridymite, iron, forsterite, and quartz (here ε is thermal expansion). As follows from Fig. 1, the coefficient of thermal expansion has an extremum for tridymite at a temperature $< 1000°$, for iron at $T < 1000°$, and for quartz at $\sim 576°$. The melting temperatures of tridymite, iron, forsterite, and quartz are, respectively, 1670, 1539, 1890, and 1470°. Thus, for tridymite, iron, and

Fig. 1. Change in thermal expansion for tridymite (a), iron ( ), forsterite ( ), and quartz ( ) (ε is in percent by volume at a temperature of 20°C)

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quartz the temperatures of the extreme values of γ are significantly lower than their melting temperatures. The question of the position of the extremum on the curve $\gamma(T)$ for forsterite remains open. However, from general physical considerations it is clear that in this case as well $T_{\text{extr}} < 1890°$. Thus, the curve $\gamma(T)$ in the case of forsterite passes through an extremum at a temperature $1200 < T < 1890°$. This means that a continuous phase transition inside the terrestrial sphere may occur at depths of 100–300 km.

Fig. 1. Change in thermal expansion for tridymite (*a*), iron (), forsterite (), and quartz () (ε is in percent of the volume at a temperature of 20°C).

It is known that regions of reduced thermodynamic stability are characterized by relatively low values of the speed of sound and high values of the absorption coefficient. At present, seismological stations reliably record a decrease in the velocities of seismic oscillations in the upper part of the mantle at depths of about 100–200 km. According to V. V. Khorosheva, the low-velocity layer in the upper part of the shell has elevated values of the absorption coefficient ([7]). Comparison of these data makes it possible to interpret the low-velocity zone in the upper part of the shell as a region of a critical or incipient transition in the mantle.

According to A. A. Luk and I. L. Nersesov, a region of reduced values of the velocity of transverse seismic oscillations is located at depths of 300–400 km beneath the Pamirs ([2]). The further discovery of new channel waves is probably a matter of time and of the accuracy of determining the velocities of seismic oscillations.

As was already shown above, in a region of reduced thermodynamic stability the coefficient of thermal expansion γ passes through a maximum. Therefore, low-velocity zones in the Earth' s shell must be a source of large thermal stresses, which in turn may be regarded as the most probable cause of the high seismic activity of our planet.

In conclusion, let us note the following. In the depths of the terrestrial shell, at different depths, there are regions in which the material is in a state close to critical. In these zones, the heated mantle material, under great pressure, has a dual nature.

Judging from the reserves of internal molecular energy, it may be regarded as a liquid under high pressure. At the same time, judging by certain physical constants—the velocity of propagation of seismic oscillations, the modulus of hardness, etc.—the material is a solid, since the distances between particles are comparatively small and their displacements, under the high forces of omnidirectional pressure, are restricted to sufficiently simple oscillatory motions. Thus, in structural terms the material is a solid. However, from the standpoint of the dynamics of the system and of the interaction of particles with one another, the material is a compressible liquid. The latter circumstance makes it possible to conclude that the displacement of material in the deep parts of the mantle in the state of critical and supercritical transitions occurs not according to the laws of plastic flow, but according to the laws of the hydrodynamics of a viscous compressible liquid. The conclusions obtained are of great significance for explaining the physical processes occurring in the depths of the planet.

Questions concerning the application of the physical conclusions obtained to problems of geology and geophysics will be considered in other works.

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Note: Figure translations are in progress. See original paper for figures.