

4. Equation of State

6. Thermal equation of state

Relations of the [pressure](#) (P), [volume](#) (V) and [temperature](#) (T), i.e. [equation of state](#) (EOS), of constituent materials are essential to discuss dynamics of [interiors of the Earth](#). Earth consists of stratified structure, which the deeper the depth, the higher the temperature and the pressure. some examples about temperature and pressure of earth interior are shown at the Table. 1..

Table. 1. some examples about temperature and pressure of earth interior

spot	Depth (km)	Temperature (K)	Pressure (Gpa)
Top of the asthenosphere	150	1700	20
660 km discontinuity	660	2000	23
Core mantle boundary	2900	4000	130

the importance of EOS at high temperature and pressure is indicated earlier, but we cannot treat the interior of earth directly due to technical difficulties. That's why interior of earth need to be reproduced in the laboratory. In the reproduction of interior of earth there are two ways to bring materials which are similar to consistent of earth's interior to high temperature and pressure. First way is HC path, which materials are first heated and then compressed, and second is CH pass, which materials are first compressed and then heated. Both ways are aimed to bring materials to high P-T conditions (P_3, V_3, T_3) from room P-T conditions (P_0, V_0, T_0).

In the way of Path HC the change of T and V in heated process is described by [thermal expansion](#), and the one of P and V in compressed one is described by [Birch-Murnaghan EOS](#). Considering Path HC, first we have to calculate condition after heating, which materials are heated, expanded, and reach the state, (P_0, V_1, T_3). After that heated expansion, materials are compressed and reach the state, (P_3, V_3, T_3). While being compressed, the higher P gets, the lower V changes. These heated and compressed process are shown in the Figure. 1..

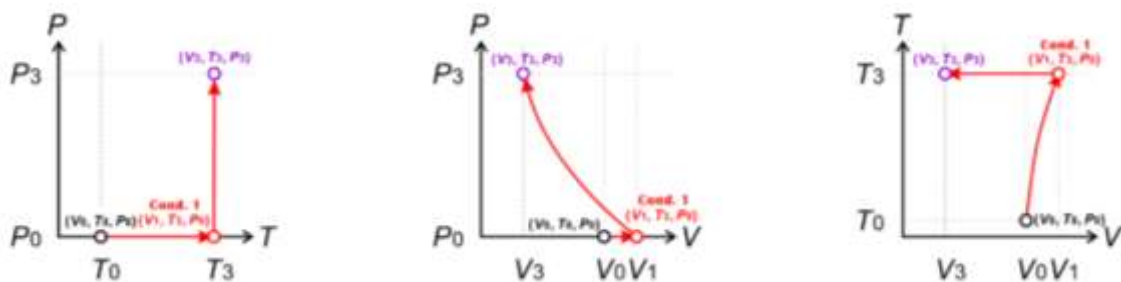


Fig. 1. The change of V, P and T in the Path HC. The materials are first heated, thermally expanded and reach to the state, (P_0, V_1, T_3) from the state, (P_0, V_0, T_0) . And then materials are compressed and reach to the state, (P_3, V_3, T_3) with constant temperature ($T = T_3$).

By assuming that [thermal expansion coefficient](#) is a linear function of T , we have following equation (4.6.1).

$$V_1 = \left\{ 1 + \sum_n \frac{\alpha_n}{n!} (T_3 - T_0)^n \right\} V_0 \quad (4.6.1)$$

Although this equation is a linear function of T , we end the thermal expansion with a second-order term of T and the equation are shown below as equation (4.6.2).

$$V_1 \cong \left\{ 1 + \alpha_0(T_3 - T_0) + \frac{1}{2}\alpha_1(T_3 - T_0)^2 \right\} V_0 \quad (4.6.2)$$

If the thermal expansion coefficients of the materials are known, equation (4.6.2) gives us the change of T and V . After thermal expansion caused by heated process, materials are compressed and reach to the state, (P_3, V_3, T_3) from (P_0, V_1, T_3) . This change is described by Birch-Murnaghan EOS.

$$P_3 - P_0 = \frac{3}{2} K_{T,0}(T_3) \left[\left(\frac{V_1}{V_3} \right)^{\frac{7}{3}} - \left(\frac{V_1}{V_3} \right)^{\frac{5}{3}} \right] \times \left\{ 1 + \frac{3}{4} (K'_{T,0} - 4) \left[\left(\frac{V_1}{V_3} \right)^{\frac{2}{3}} - 1 \right] \right\} \quad (4.6.3)$$

If the initial state (P_0, V_1, T_3) , $K_{T,0}(T_3)$ and $K'_{T,0}$ are known, equation (4.6.3) gives us the change of P and V . $K_{T,0}(T)$ is the [isothermal bulk modulus](#) at zero P as a function of T , and it is assumed a linear function of T . To express $K_{T,0}(T)$ simply it is ended with first order term of T and as a result $K_{T,0}(T_3)$ is described as equation (4.6.4).

$$K_{T,0}(T_3) \cong K_{T,0}(T_0) + \left(\frac{\partial K_{T,0}}{\partial T} \right)_P (T_3 - T_0) \quad (4.6.4)$$

Thanks to equation (4.6.4) we can get $K_{T,0}(T_3)$, and the last unknown factor is $K'_{T,0}$. $K'_{T,0}$ is usually assumed to $\left(\frac{\partial K_{T,0}}{\partial P} \right)_T$, which is independent from P and T .

$$K'_{T,0} = \left(\frac{\partial K_{T,0}}{\partial P} \right)_T \quad (4.6.5)$$

Equation (4.6.3) ~ (4.6.5) gives us the changes of P and V in the process of compression.

In the way of Path CH the change of P and V in compressed process is described by Birch-Murnaghan EOS, and the one of P and T in heated one is described by [Mie-Grüneisen EOS](#). Considering Path CH, first we have to calculate condition after compression, which materials are compressed and reach the state, (P_2, V_3, T_0) . After compression, materials are heated and reach

the state, (P_3, V_3, T_3) . While being compressed, the higher P gets, the lower V changes, and while being heated, the higher T gets, the higher P changes to keep V constant. These compressed and heated process are shown in the Figure. 2..

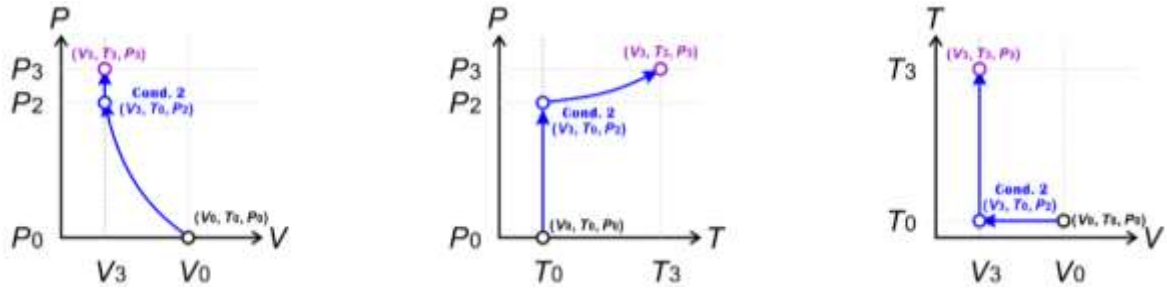


Fig. 2. The change of V, P and T in the Path CH. The materials are first compressed with constant temperature ($T=T_0$) and reached to (P_2, V_3, T_0) from (P_0, V_0, T_0) . And then materials are heated with constant volume ($V=V_3$).

Although materials are first compressed, The process of compression from (P_0, V_0, T_0) to (P_2, V_3, T_0) with constant temperature ($T=T_0$) is described by Birch-Murnaghan EOS and it is shown by equation (4.6.6).

$$P_2 - P_0 = \frac{3}{2} K_{T,0}(T_0) \left[\left(\frac{V_0}{V_3} \right)^{\frac{7}{3}} - \left(\frac{V_0}{V_3} \right)^{\frac{5}{3}} \right] \times \left\{ 1 + \frac{3}{4} (K'_{T,0} - 4) \left[\left(\frac{V_0}{V_3} \right)^{\frac{2}{3}} - 1 \right] \right\} \quad (4.6.6)$$

With respect to $K'_{T,0}$ please refer equation (4.6.5). Thanks to equation (4.6.6) we can get the result of the change in pressure and volume due to compression and next we consider the heated process. The change of P related to E increase by T increase at constant V is described Mie-Grüneisen equation of state, using the [Grüneisen parameter](#) (γ_{th}). This change from (P_2, V_3, T_0) to (P_3, V_3, T_3) shown by equation (4.6.7).

$$\Delta P_{th} = P_3 - P_2 = \gamma_{th} (\Delta E_{th} / V_3) \quad (4.6.7)$$

From Gruneisen's relationship between the coefficient of thermal expansion α and the [specific heat capacity](#) C_v I lead equation (4.6.7).

$$\begin{aligned} \alpha &= \frac{\gamma C_v}{3\kappa V} \\ (3\alpha)\kappa &= \frac{\gamma C_v}{V} \\ \left\{ \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \right\} \left\{ -V \left(\frac{\partial P}{\partial V} \right)_T \right\} &= \frac{\gamma C_v}{V} \\ - \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial P}{\partial V} \right)_T &= \frac{\gamma C_v}{V} \end{aligned} \quad (4.6.8)$$

The following equation (4.6.9) is established from the relationship of partial derivatives of three variables $(\frac{\partial V(T,P)}{\partial T})_P$, $(\frac{\partial P(T,V)}{\partial V})_T$, $(\frac{\partial T(V,P)}{\partial P})_V$.

$$\left(\frac{\partial V(T,P)}{\partial T}\right)_P \left(\frac{\partial P(T,V)}{\partial V}\right)_T \left(\frac{\partial T(V,P)}{\partial P}\right)_V = -1 \quad (4.6.9)$$

From equation (4.6.8) and (4.6.9), equation (4.6.7) can be lead.

$$\left\{-\left(\frac{\partial T(V,P)}{\partial P}\right)_V\right\}^{-1} = \frac{\gamma C_v}{V}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\gamma C_v}{V}$$

$$\int_{T_0}^{T_3} dP = \int_{T_0}^{T_3} \frac{\gamma C_v}{V} dT$$

$$\int_{T_0}^{T_3} dP = \int_{T_0}^{T_3} \frac{\gamma C_v}{V} dT$$

$$P_3 - P_2 = \gamma_{th} (\Delta E_{th}/V_3) \quad (4.6.7)$$

In the process of leading equation (4.6.7) we use C_v , and if we know C_v , we can ask for the value of P_3 . From the results of the specific heat of solids by the [Debye model](#), using the [Debye temperature](#), the specific heat can be expressed as follows equation (4.6.10).

$$C_v = 9Nk_B \left(\frac{T^3}{\theta_D}\right)^3 \int_{\theta_D/T_0}^{\theta_D/T_3} \{x^4 \exp x / (\exp x - 1)^2\} dx \quad (4.6.10)$$

Equation (4.6.7) and (4.6.10) gives us the changes of P and T in the heated process with constant V.

It is not settled whether the HC pass or the CH pass is better. However some scientist say that the high-temperature Birch-Murnaghan EOS does not have physical meaning, but the Mie-Grüneisen-Debye EOS does. And in the respect that physical property under high temperature and room pressure conditions is more difficult than that under High pressure and room temperature the CH pass is better than the HC pass.