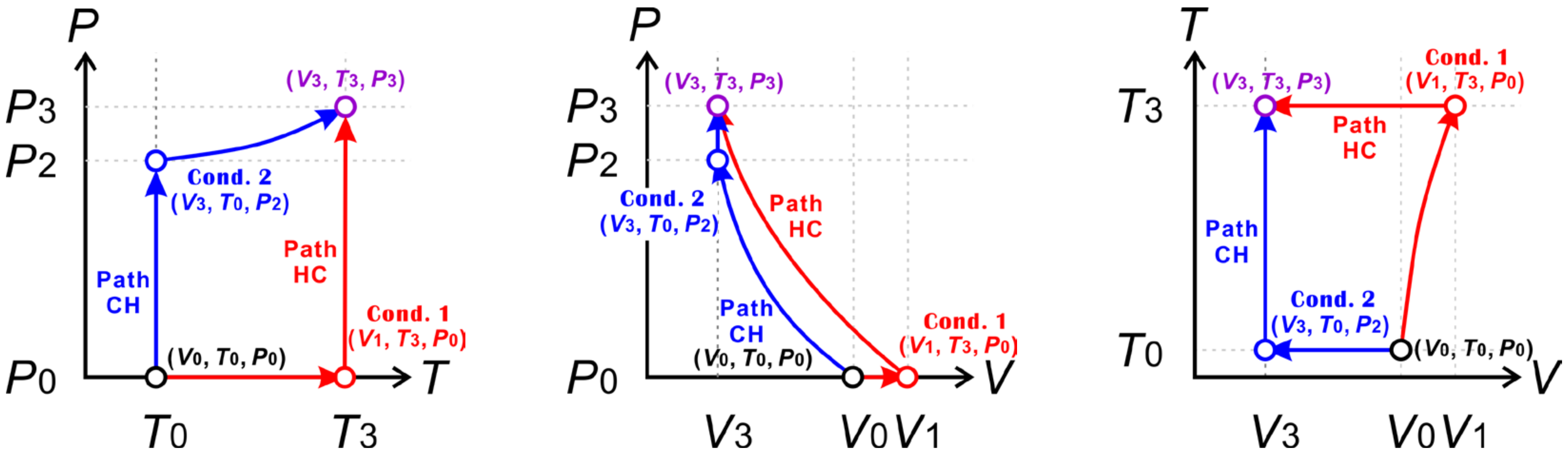
Mineral Physics I
Chapter 4. Equation of State
Section 6. Thermal equation of state

Thermal equation of state

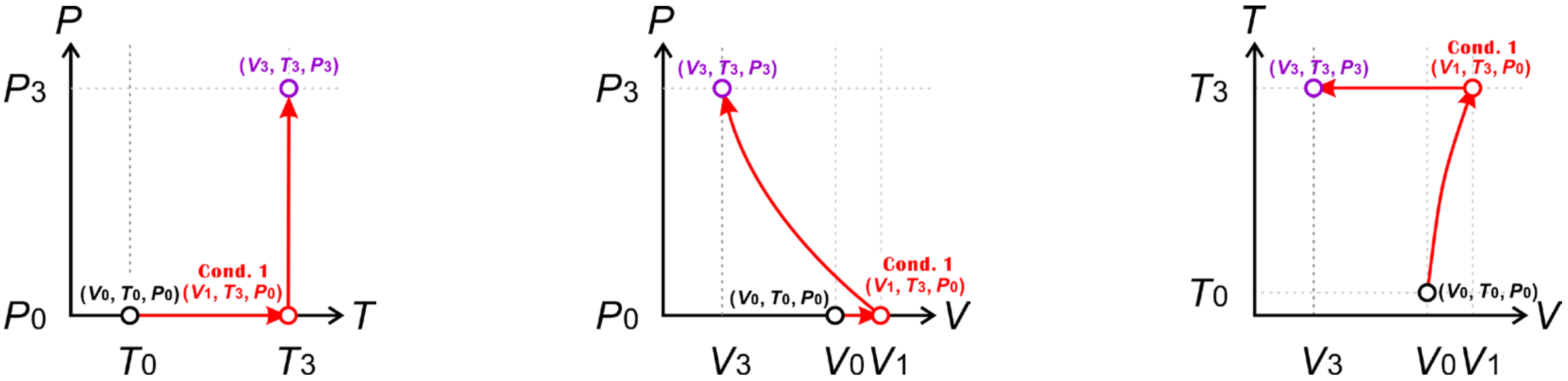
- Thermal equation of state: an equation of state including T as well as P.
- Thermal equation of state is essential for geophysics, because the planetary interiors are under high temperature conditions
  - ✓ Top of the asthenosphere: 1700 K
  - ✓ 660-km discontinuity: 2000 K
  - ✓ Core-mantle boundary: 4000~5000 K

Paths HC and CH



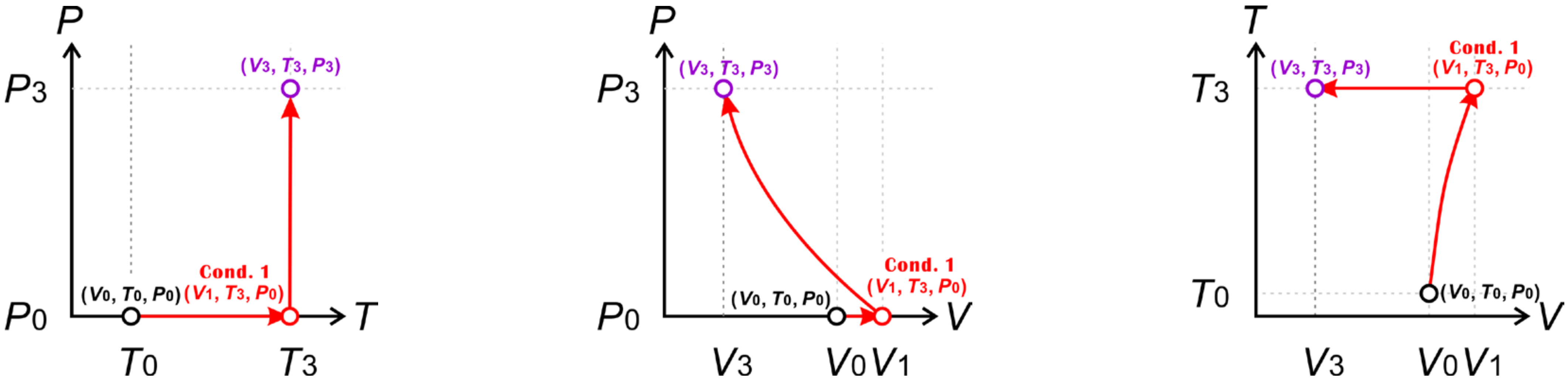
- Two paths to reach high P-T conditions (P_3, V_3, T_3) from ambient conditions of (P_0, V_0, T_0)
  - ✓ HC path: first heated then compressed
  - ✓ CH path: first compressed then heated

Path HC:
HT Birch-Murnaghan EOS -1



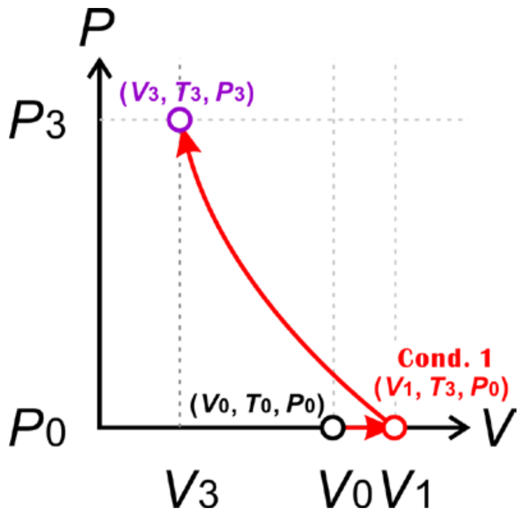
- V increases from V_0 to V_1 by heating from T_0 to T_3 at the initial pressure P_0 due to thermal expansion.
  - ✓ $V_1 = V_0 \int_{T_0}^{T_3} \alpha(T)$ (4.6.1)
    - α: thermal expansion coefficient

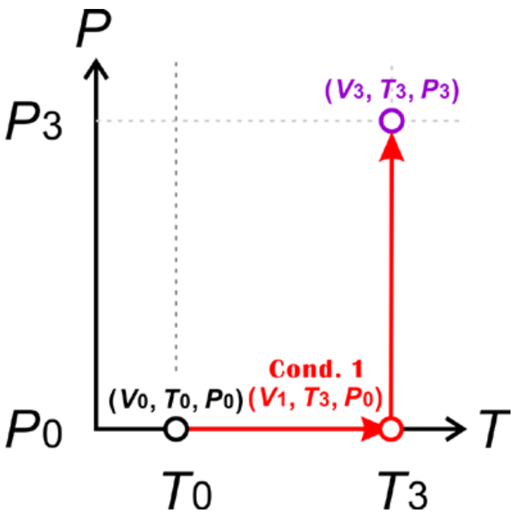
Path HC:
HT Birch-Murnaghan EOS -2

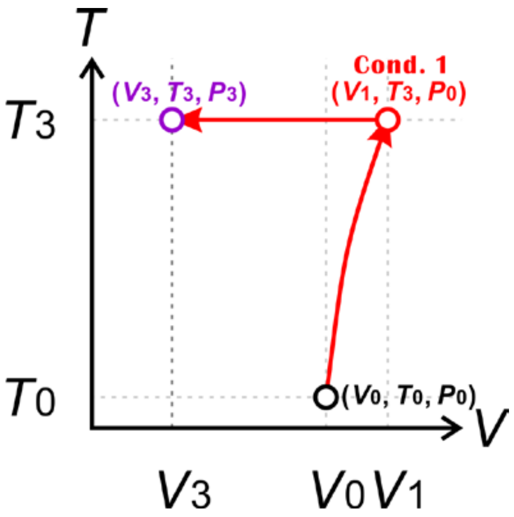


- Assuming the constant thermal expansion coefficient α_0, we have
  - ✓ $V_1 \cong \{1 + \alpha_0(T_3 - T_0)\}V_0$ (4.6.2)
- By assuming that thermal expansion coefficient is a linear function of T, we have
  - ✓ $V_1 \cong \left\{1 + \alpha_0(T_3 - T_0) + \frac{1}{2}\alpha_1(T_3 - T_0)^2\right\}V_0$ (4.6.3)

Path HC:
HT Birch-Murnaghan EOS -3





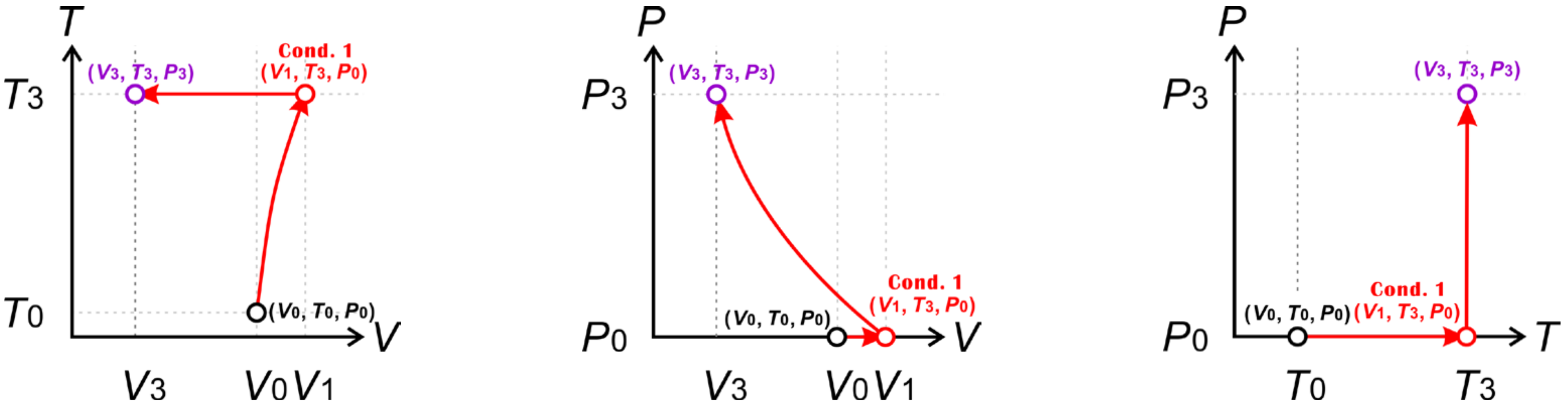


- Compression from V_1 to V_3 to increase P from P_0 to P_3 expressed by high-temperature 3rd-order Birch-Murnaghan EOS

✓ $$P_3 - P_0 = \frac{3}{2}K_{T,0}(T_3)\left[\left(\frac{V_1}{V_3}\right)^{\frac{7}{3}} - \left(\frac{V_1}{V_3}\right)^{\frac{5}{3}}\right] \times \left\{1 + \frac{3}{4}\left(K'_{T,0} - 4\right)\left[\left(\frac{V_1}{V_3}\right)^{\frac{2}{3}} - 1\right]\right\} \quad (4.6.4)$$

- $K_{T,0}(T)$ is the isothermal bulk modulus at zero P as a function of T

Path HC:
HT Birch-Murnaghan EOS -4

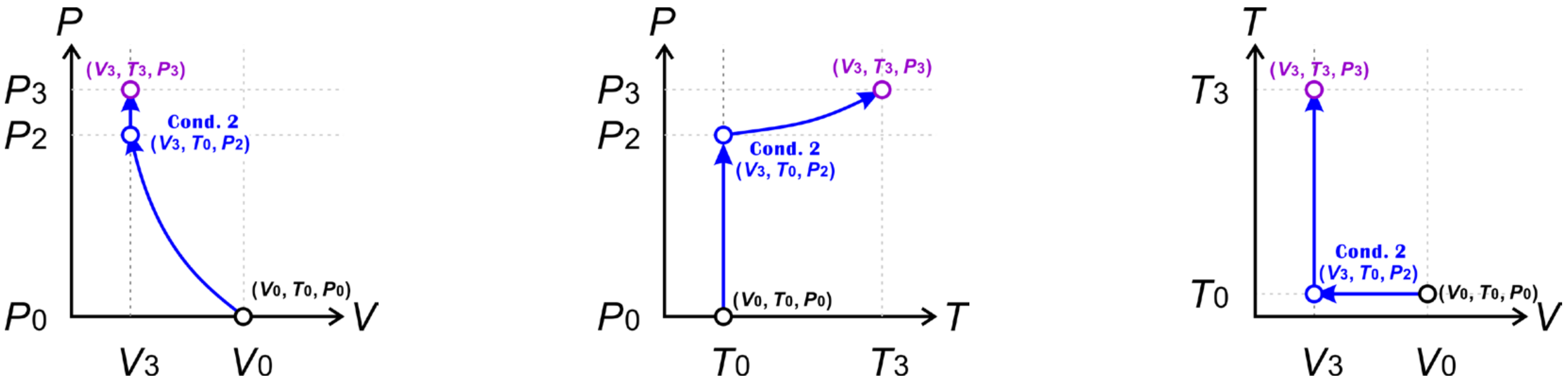


➢For simplicity, $K_{T,0}(T)$ is assumed a linear function of T

✓$K_{T,0}(T_3) \cong K_{T=T_0,0} + \left(\frac{\partial K_{T,0}}{\partial T}\right)_P (T_3 - T_0)$ (4.6.5)

Because of experimental difficulty, $K'_{T,0} = \left(\frac{\partial K_{T,0}}{\partial P}\right)_T$ is usually assumed independent from P and T

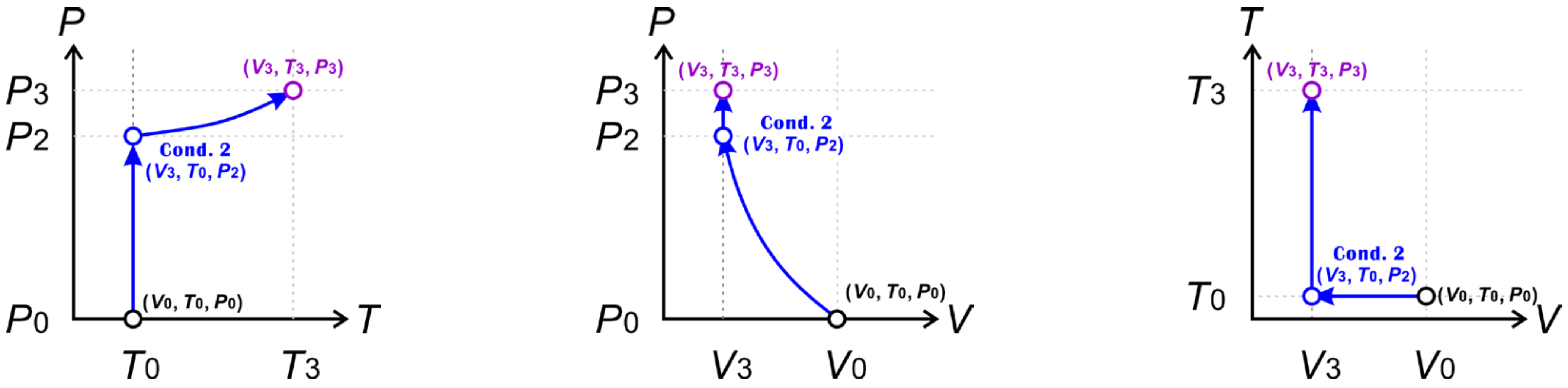
Path CH:
Mie-Grüneisen equation of state -1



- V is first decreased from V_0 to V_3 at $T = T_0$ to increase P from P_0 to P_2

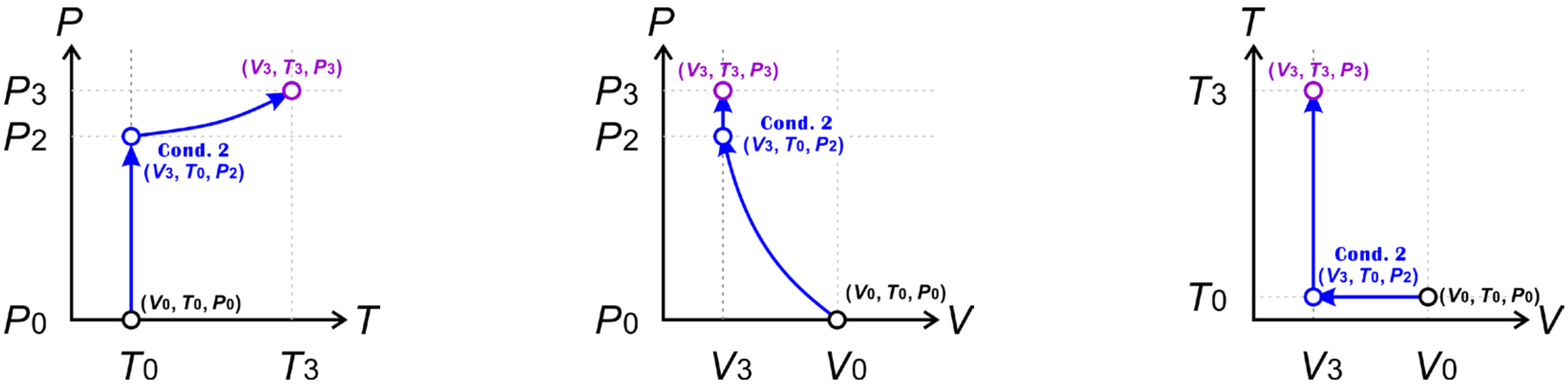
✓ $P_2 - P_0 = \frac{3}{2} K_{T,0}(T_0) \left[\left(\frac{V_0}{V_3}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V_3}\right)^{\frac{5}{3}} \right] \times \left\{ 1 + \frac{3}{4} \left(K'_{T,0} - 4\right) \left[\left(\frac{V_0}{V_3}\right)^{\frac{2}{3}} - 1 \right] \right\}$ (4.6.6)

Path CH:
Mie-Grüneisen-EOS -2



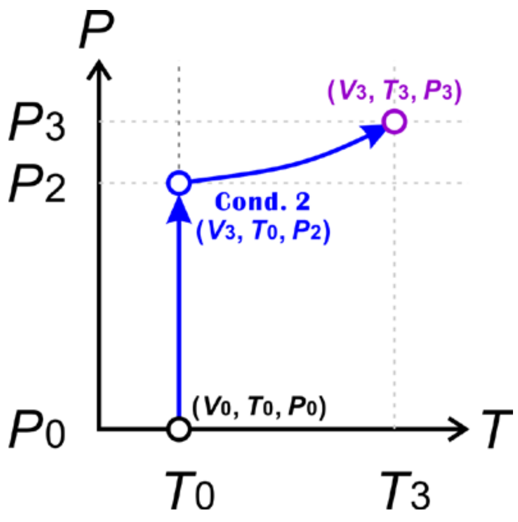
- P increase $\Delta P_{\text{th}} = P_3 - P_2$ by T increase at constant volume $V = V_3$
  - ✓ $\Delta P_{\text{th}} = P_3 - P_2 = \int_{T_0}^{T_3} \left(\frac{\partial P}{\partial T}\right)_{V=V_3} \mathrm{d}T$ (4.6.7)
    - $(\partial P/\partial T)_V$: thermal pressure

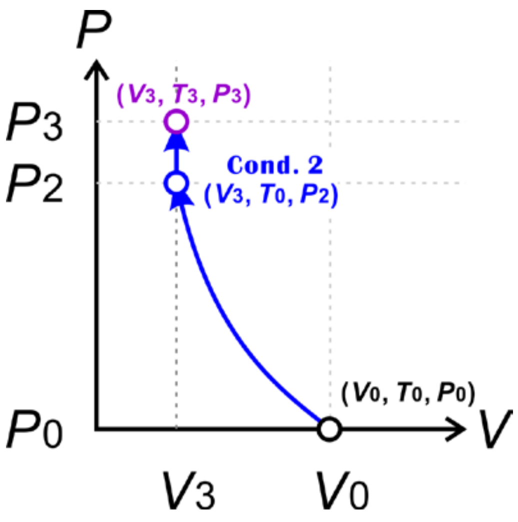
Path CH:
Mie-Grüneisen-EOS -3

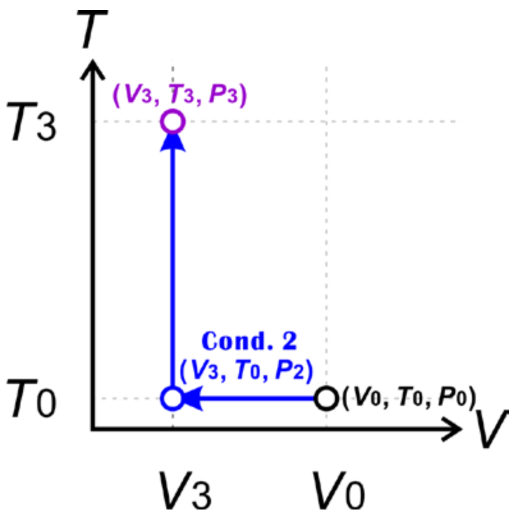


- ΔP_{th}: related to E increase by T increase at constant V
  - ✓ $\Delta P_{\mathrm{th}} = \gamma_{\mathrm{th}}(\Delta E_{\mathrm{th}}/V)$ (4.6.8)
    - γ_{th}: Grüneisen parameter
      - Definition of γ
    - Eq. (4.6.8): **Mie-Grüneisen equation of state**

Path CH: Mie-Grüneisen-EOS -4







- $\Delta E_{\rm th}$ is expressed by isochoric heat capacity C_V:
  - ✓ $\Delta E_{\rm th} = \int_{T_0}^{T_3} C_V \mathrm{d}T$ (4.6.9)
- By the Debye approximation,
  - ✓ $C_V = 9Nk_B(T/\Theta_{\rm D})^3 \int_{\Theta_{\rm D}/T_0}^{\Theta_{\rm D}/T_3} \{x^4 \exp x/(\exp x - 1)^2\}\mathrm{d}x$ (3.7.18')

Path HC or CH?

- Which is better, Path HC or CH?
  - ✓ Although some one says that the high-temperature Birch-Murnaghan EOS does not have physical meaning, but the Mie-Grüneisen-Debye EOS does, however, …?
- Merits of CH path
  - ✓ Physical properties under HT and RP conditions for the HC path are more difficult to obtain those under HP and RT conditions for the CH path
  - ✓ The thermal pressure for the CH path is more easily estimated due to the Debye model than high-temperature compression for the HC path

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End