Rules for partial derivatives

Using

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz.$$

in

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz,$$

gives

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left[\left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz\right] + \left(\frac{\partial x}{\partial z}\right)_y dz$$

Noting that the formula we arrive at should be valid for any (small) dx and dz one finds two different equations:

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y, \quad \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1. \tag{1}$$

Some material parameters

We have the thermal expansion coefficient

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P,$$

and the isothermal compressibility

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

For water they are known to be

- $\beta \approx 2.57 \times 10^{-4}\ \mathrm{K}^{-1}$,
- $\kappa_T \approx 4.52 \times 10^{-10}\ \mathrm{Pa}^{-1}$.

Experiment at constant pressure?

We now want to illustrate that it is very difficult to perform experiments on liquids and solids at constant volume.
To this end we will determine $\left(\frac{\partial P}{\partial T}\right)_V$ for water, which tells us how fast the pressure increases with temperature when the volume is fixed. Eq. (1) gives:

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = \frac{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P}{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\beta}{\kappa_T}.$$

With the numerical values above we find

$$\frac{\beta}{\kappa_T} \approx 5.7 \times 10^5\ \mathrm{Pa/K} = 5.7\ \mathrm{atm/K},$$

which implies that already an increase of the temperature of the water by 1 K would demand a pressure increase of 5.7 atm, to prevent it from expanding.