

MEASURING HEAT CAPACITY AT CONSTANT VOLUME

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Heat capacities of substances can be measured at constant volume or constant pressure. To measure the heat capacity of a gas, it is relatively easy to keep the gas at a constant volume (just enclose it in a sealed container). For solids and liquids, however, it is much easier to measure heat capacity at constant pressure. To see why, we can estimate how much pressure needs to be increased to keep a solid or liquid from expanding as it is heated.

The thermal expansion coefficient is a measure of the relative volume change with temperature at constant pressure:

$$\beta \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (1)$$

Suppose we heat a solid (or liquid) a bit at constant pressure, so that its volume changes by an amount dV :

$$dV = \beta V dT \quad (2)$$

The reciprocal of the bulk modulus is the *isothermal compressibility*:

$$\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (3)$$

This measures how much the relative volume changes as we increase the pressure at constant temperature. If we take the substance that we heated a bit and then compress it at the new temperature by just the amount that it expanded, then the volume change is $-dV$ so

$$dV = \kappa_T V dP \quad (4)$$

Dividing 4 by 2 we get the derivative of pressure with respect to temperature at constant volume, since after the two actions, the volume is unchanged:

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{\beta}{\kappa_T} = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} \quad (5)$$

For an ideal gas, we have

$$\beta = \frac{1}{V} \frac{Nk}{P} \quad (6)$$

$$\kappa_T = \frac{NkT}{VP^2} = \frac{1}{P} \quad (7)$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{Nk}{V} = \frac{\beta}{\kappa_T} \quad (8)$$

For water, the values given by Schroeder are (at 25° C):

$$\beta = 2.57 \times 10^{-4} \text{ K}^{-1} \quad (9)$$

$$\kappa_T = 4.52 \times 10^{-10} \text{ Pa}^{-1} \quad (10)$$

To keep the volume of some water constant as its temperature is raised from 20° C to 30° C, the pressure would need to be increased by about

$$\Delta P \cong \frac{\beta}{\kappa_T} \Delta T = \frac{2.57 \times 10^{-4}}{4.52 \times 10^{-10}} \times 10 = 5.69 \times 10^6 \text{ Pa} \approx 56 \text{ atm} \quad (11)$$

For mercury in the same temperature range

$$\beta = 1.81 \times 10^{-4} \text{ K}^{-1} \quad (12)$$

$$\kappa_T = 4.04 \times 10^{-11} \text{ Pa}^{-1} \quad (13)$$

so the pressure increase must be

$$\Delta P \cong \frac{\beta}{\kappa_T} \Delta T = \frac{1.81 \times 10^{-4}}{4.04 \times 10^{-11}} \times 10 = 4.48 \times 10^7 \text{ Pa} \approx 442 \text{ atm} \quad (14)$$

To measure C_V thus requires very large pressures for typical liquids (and even more so for solids). Measuring C_P for liquids and solids is relatively easy as we can just heat them at atmospheric pressure.