Compressibility, expansion coefficient

a. Compressibility means "capable of being compressed". If the pressure increases by a small amount Δp , (and the temperature doesn't change) then the volume changes by the small amount

$$\Delta V \approx -V\kappa_T \Delta p$$

We certainly expect that if the pressure increases the volume will decrease, so the negative sign acts to make κ_T a positive quantity.

If κ_T is small then a given Δp will result in a small shrinkage ΔV : the material is *hard*. If κ_T is large then a given Δp will result in a large shrinkage ΔV : the material is *soft*.

A substance with high compressibility is also called "squeezable".

The factor of 1/V was put into the definition because the shrinkage is proportional to the volume. Divide by volume to remove this dependence, which makes κ_T a property of the *substance* rather than of the *sample*.

b. The expansion coefficient β is negative for water between 0°C and 4°C.

c. In two-phase coexistence (i.e. at the cliffs in the graphs below) $\kappa_T = +\infty$ and $\beta = \pm\infty$.



d. For the ideal gas,
$$\kappa_T(p,T) = \frac{1}{p}$$
 and $\beta(p,T) = \frac{1}{T}$.
e.

$$\frac{\partial \beta}{\partial p} = \frac{1}{V} \frac{\partial^2 V}{\partial p \partial T} - \frac{1}{V^2} \frac{\partial V}{\partial p} \frac{\partial V}{\partial T}$$
$$\frac{\partial \kappa_T}{\partial p} = -\frac{1}{V} \frac{\partial^2 V}{\partial T \partial p} + \frac{1}{V^2} \frac{\partial V}{\partial T} \frac{\partial V}{\partial p}$$

which together imply

$$\frac{\partial \kappa_T(p,T)}{\partial T} = -\frac{\partial \beta(p,T)}{\partial p}$$

f. For the ideal gas, $\frac{\partial \kappa_T(p,T)}{\partial T} = 0$ and $\frac{\partial \beta(p,t)}{\partial p} = 0$. Note: Watch out for this error!

$$\kappa_T = \frac{1}{p} = \frac{V}{Nk_BT}$$
$$\frac{\partial \kappa_T}{\partial T} = -\frac{V}{Nk_BT^2} = -\frac{Nk_B}{p^2V}.$$

This error comes from considering κ_T as a function of V and T, whereas it is defined (and measured!) as a function of p and T. (A measurement of κ_T is performed on a sample at some given pressure — usually atmospheric pressure. It is *not* performed on some sample in a strong box of fixed volume!)