Isothermal *vs.* adiabatic compressibility

a. We start with the relation

$$dS = \frac{\partial S}{\partial T}\bigg)_p dT + \frac{\partial S}{\partial p}\bigg)_T dp$$

and find "conventional names" for the partial derivatives. First, by the definition of heat capacity, we have

$$\frac{\partial S}{\partial T}\bigg)_p = \frac{C_p}{T}.$$

Then, using the Maxwell relation associated with $G(T, p)$,

$$\frac{\partial S}{\partial p}\bigg)_T = -\frac{\partial V}{\partial T}\bigg)_p = -V\beta.$$

Together these become

$$dS = \frac{C_p}{T}\, dT - V\beta\, dp$$

The above equation holds for *any* small change in T and p. If we restrict it to a small change at constant S, that is, a change with $dS = 0$, we find
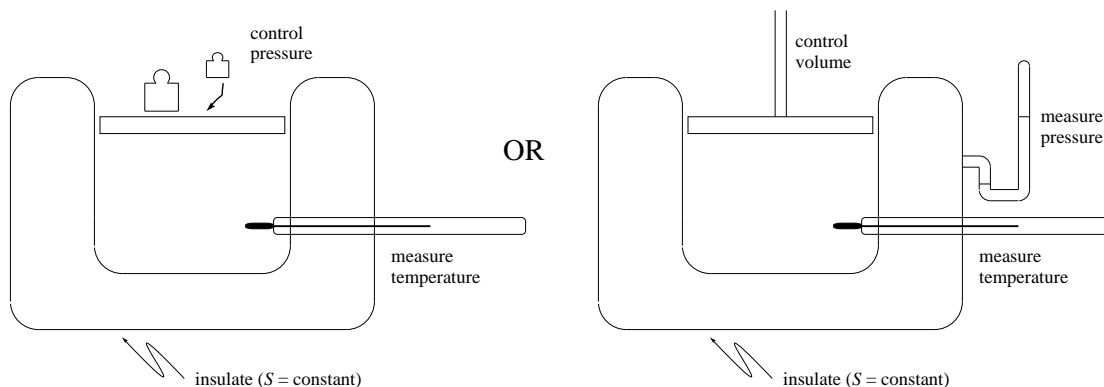
$$\frac{C_p}{T}\, dT = V\beta\, dp$$

or

$$\frac{\partial T}{\partial p}\bigg)_S = \frac{\beta T}{C_p/V}.$$

(I write the fraction in this perhaps-contorted form to make it apparent that it is intensive.)

Two experiments that measure this quantity directly are sketched below.

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b. Start with:

$$dV = \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT.$$

Restrict to a change at constant S, and divide by dp:

$$\left(\frac{\partial V}{\partial p}\right)_S = \left(\frac{\partial V}{\partial p}\right)_T + \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_S.$$

Divide both sides by $-V$:

$$-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T - \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \frac{\beta T}{C_p/V}.$$

Recognize the definitions of κ_S, κ_T, and β in the above:

$$\kappa_S = \kappa_T - \frac{\beta^2 T}{C_p/V}.$$

c.

$$\gamma \equiv \frac{C_p}{C_V} = \left[T\left(\frac{\partial S}{\partial T}\right)_p\right] \Big/ \left[T\left(\frac{\partial S}{\partial T}\right)_V\right] = \left[\left(\frac{\partial S}{\partial T}\right)_p\right] \Big/ \left[\left(\frac{\partial S}{\partial T}\right)_V\right].$$

Use the implicit function theorem to find

$$\gamma = \left[-\left(\frac{\partial p}{\partial T}\right)_S \Big/ \left(\frac{\partial p}{\partial S}\right)_T\right] \Big/ \left[-\left(\frac{\partial V}{\partial T}\right)_S \Big/ \left(\frac{\partial V}{\partial S}\right)_T\right],$$

then rearrange algebraically giving

$$\gamma = \left[\left(\frac{\partial p}{\partial T}\right)_S \Big/ \left(\frac{\partial V}{\partial T}\right)_S\right] \Big/ \left[\left(\frac{\partial p}{\partial S}\right)_T \Big/ \left(\frac{\partial V}{\partial S}\right)_T\right].$$

This rearrangement has the benefit that now the derivatives within the first square brackets are with respect to T alone, while the derivatives within the second square brackets are with respect to S alone, so within either set of square brackets we can use the rules of single-variable calculus. Namely use the inverse rule followed by the chain rule, followed by the inverse rule a second time to find

$$\begin{aligned}
\gamma &= \left[\left(\frac{\partial p}{\partial T}\right)_S \left(\frac{\partial T}{\partial V}\right)_S\right] \Big/ \left[\left(\frac{\partial p}{\partial S}\right)_T \left(\frac{\partial S}{\partial V}\right)_T\right] \\
&= \left[\left(\frac{\partial p}{\partial V}\right)_S\right] \Big/ \left[\left(\frac{\partial p}{\partial V}\right)_T\right] \\
&= \left[\left(\frac{\partial V}{\partial p}\right)_T\right] \Big/ \left[\left(\frac{\partial V}{\partial p}\right)_S\right] \\
&= \left[-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T\right] \Big/ \left[-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S\right].
\end{aligned}$$

And in this form we immediately recognize the adiabatic and isothermal compressibilities:

$$\gamma \equiv \frac{C_p}{C_V} = \frac{\kappa_T}{\kappa_S}.$$

The argument above came from students in the Statistical Mechanics class of Spring 2017. My own argument is given in the paragraph below. I like the students's argument better than mine, even though it's longer, because it goes straight to the heart of the calculus involved, whereas my argument relies on the names of various derivatives. Here's my argument:

From class,

$$C_p = C_V + TV\frac{\beta^2}{\kappa_T},$$

so

$$\begin{aligned}
C_p \kappa_S &= C_p\left(\kappa_T - \frac{\beta^2 T}{C_p/V}\right) \\
&= C_p \kappa_T - \beta^2 TV \\
&= \left(C_V + TV\frac{\beta^2}{\kappa_T}\right)\kappa_T - \beta^2 TV \\
&= C_V \kappa_T + TV\beta^2 - \beta^2 TV \\
&= C_V \kappa_T.
\end{aligned}$$

Thus

$$\gamma \equiv \frac{C_p}{C_V} = \frac{\kappa_T}{\kappa_S}.$$

Regardless of which argument you prefer, the result is staggering: The experiments used to measure C_p and C_V are wildly different from the experiments used to measure κ_T and κ_S. The heat capacities involve the response of temperature to heat, whereas the compressibilites involve the response of volume to pressure ("hardness" or "softness"). How could these *possibly* be connected? And yet they are. If you discovered a substance for which these two ratios were *not* equal, then you could use that substance to build a perpetual motion machine. To quote Faraday, "Nothing is too wonderful to be true."