Isothermal *vs.* adiabatic compressibility

a. We start with the relation

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

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

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

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

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

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

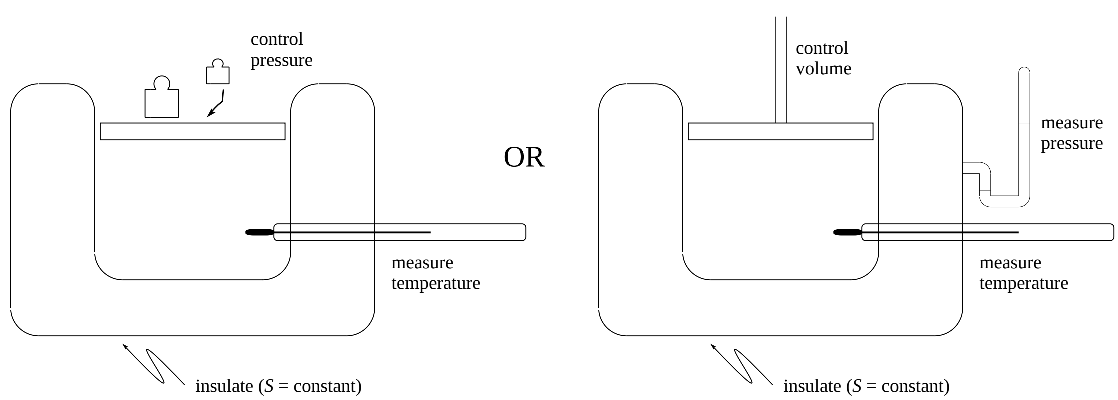
$$\frac{C_p}{T}\, dT = V\beta\, dp$$

or

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

(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.



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. 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

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