

## ISOTHERMAL AND ISENTROPIC COMPRESSIBILITIES

Link to: [physicspages home page](#).

To leave a comment or report an error, please use the auxiliary blog.

Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 5.16.

An expression similar to that relating the heat capacities can be derived to relate the isothermal and isentropic compressibilities  $\kappa_T$  and  $\kappa_S$ , defined as

$$(0.1) \quad \kappa_T \equiv -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

$$(0.2) \quad \kappa_S \equiv -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_S$$

These quantities measure the fractional change in volume of a substance in response to a change in pressure. To obtain the relation between them, we use a method similar to that for heat capacities  $C_V$  and  $C_P$ .

If we write  $S = S(P, T)$  then

$$(0.3) \quad dS = \left( \frac{\partial S}{\partial P} \right)_T dP + \left( \frac{\partial S}{\partial T} \right)_P dT$$

Also, starting with  $V = V(P, S)$  we have

$$(0.4) \quad dV = \left( \frac{\partial V}{\partial P} \right)_S dP + \left( \frac{\partial V}{\partial S} \right)_P dS$$

Substituting 0.3 into 0.4 we get

$$(0.5) \quad dV = \left[ \left( \frac{\partial V}{\partial S} \right)_P \left( \frac{\partial S}{\partial P} \right)_T + \left( \frac{\partial V}{\partial P} \right)_S \right] dP + \left( \frac{\partial V}{\partial T} \right)_P dT$$

At constant temperature  $dT = 0$  and we get

$$(0.6) \quad \left( \frac{\partial V}{\partial P} \right)_T = \left( \frac{\partial V}{\partial S} \right)_P \left( \frac{\partial S}{\partial P} \right)_T + \left( \frac{\partial V}{\partial P} \right)_S$$

$$(0.7) \quad -V\kappa_T = \left( \frac{\partial V}{\partial S} \right)_P \left( \frac{\partial S}{\partial P} \right)_T - V\kappa_S$$

From the Maxwell relation from the Gibbs energy

$$(0.8) \quad \left( \frac{\partial S}{\partial P} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_P$$

Also, from the definition of the thermal expansion coefficient  $\beta$

$$(0.9) \quad \beta \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

Combining these last two equations gives

$$(0.10) \quad -V\kappa_T = -\beta V \left( \frac{\partial V}{\partial S} \right)_P - V\kappa_S$$

To get rid of the last partial derivative, we observe that the volume change  $dV$  due to a temperature change  $dT$  at constant pressure is

$$(0.11) \quad dV = \beta V dT$$

The entropy change due to an influx of heat  $dQ$  at constant pressure at temperature  $T$  is

$$(0.12) \quad dS = \frac{dQ}{T}$$

$$(0.13) \quad = C_P \frac{dT}{T}$$

Dividing these two relations gives

$$(0.14) \quad \left( \frac{\partial V}{\partial S} \right)_P = \frac{TV\beta}{C_P}$$

Inserting this into 0.10 and cancelling off a factor of  $-V$  gives the final result

$$(0.15) \quad \kappa_T = \kappa_S + \frac{TV\beta^2}{C_P}$$

For an ideal gas, we can use this equation to work out  $\kappa_S$ :

$$(0.16) \quad \beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \frac{Nk}{PV} = \frac{1}{T}$$

$$(0.17) \quad \kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = \frac{NkT}{P^2V} = \frac{1}{P}$$

$$(0.18) \quad C_P = C_V + Nk$$

$$(0.19) \quad = Nk \left( 1 + \frac{f}{2} \right)$$

$$(0.20) \quad \kappa_S = \frac{1}{P} - \frac{V}{NkT \left( 1 + \frac{f}{2} \right)}$$

$$(0.21) \quad = \frac{1}{P} \frac{f}{f+2}$$

where in the third line, we've used Schroeder's equation 1.48, and  $f$  is the number of degrees of freedom of each gas molecule.

To check this, recall that for an isentropic (adiabatic) process in an ideal gas

$$(0.22) \quad PV^\gamma = K$$

$$(0.23) \quad V = \left( \frac{K}{P} \right)^{1/\gamma}$$

where  $\gamma = (f+2)/f$  and  $K$  is a constant. So

$$(0.24) \quad \kappa_S = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_S$$

$$(0.25) \quad = -\left( \frac{P}{K} \right)^{1/\gamma} \left( -\frac{1}{\gamma} \right) \left( \frac{K}{P} \right)^{1/\gamma} \frac{1}{P}$$

$$(0.26) \quad = \frac{1}{P\gamma} = \frac{1}{P} \frac{f}{f+2}$$

which is the same as 0.21, so equation 0.15 checks out for an ideal gas.

PINGBACKS

Pingback: Van der Waals fluid at the critical point