ISOTHERMAL AND ISENTROPIC COMPRESSIBILITIES

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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 κ_T and κ_S, defined as

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

$$\kappa_S \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S \tag{2}$$

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

$$dS=\left(\frac{\partial S}{\partial P}\right)_T dP+\left(\frac{\partial S}{\partial T}\right)_P dT \tag{3}$$

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

$$dV=\left(\frac{\partial V}{\partial P}\right)_S dP+\left(\frac{\partial V}{\partial S}\right)_P dS \tag{4}$$

Substituting 3 into 4 we get

$$dV=\left[\left(\frac{\partial V}{\partial S}\right)_P\left(\frac{\partial S}{\partial P}\right)_T+\left(\frac{\partial V}{\partial P}\right)_S\right]dP+\left(\frac{\partial V}{\partial T}\right)_P dT \tag{5}$$

At constant temperature $dT=0$ and we get

$$\left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\partial V}{\partial S}\right)_P\left(\frac{\partial S}{\partial P}\right)_T+\left(\frac{\partial V}{\partial P}\right)_S \tag{6}$$

$$-V\kappa_T = \left(\frac{\partial V}{\partial S}\right)_P\left(\frac{\partial S}{\partial P}\right)_T-V\kappa_S \tag{7}$$

From the Maxwell relation from the Gibbs energy

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{8}$$

Also, from the definition of the thermal expansion coefficient β

$$\beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{9}$$

Combining these last two equations gives

$$-V\kappa_T = -\beta V\left(\frac{\partial V}{\partial S}\right)_P - V\kappa_S \tag{10}$$

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

$$dV = \beta V\, dV \tag{11}$$

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

$$dS = \frac{dQ}{T} \tag{12}$$

$$= C_P \frac{dT}{T} \tag{13}$$

Dividing these two relations gives

$$\left(\frac{\partial V}{\partial S}\right)_P = \frac{TV\beta}{C_P} \tag{14}$$

Inserting this into 10 and cancelling off a factor of $-V$ gives the final result

$$\kappa_T = \kappa_S + \frac{TV\beta^2}{C_P} \tag{15}$$

For an ideal gas, we can use this equation to work out κ_S:

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{Nk}{PV} = \frac{1}{T} \tag{16}$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{NkT}{P^2 V} = \frac{1}{P} \tag{17}$$

$$C_P = C_V + Nk \tag{18}$$

$$= Nk\left(1+\frac{f}{2}\right) \tag{19}$$

$$\kappa_S = \frac{1}{P} - \frac{V}{NkT\left(1+\frac{f}{2}\right)} \tag{20}$$

$$= \frac{1}{P}\frac{f}{(f+2)} \tag{21}$$

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

$$PV^\gamma = K \tag{22}$$

$$V = \left(\frac{K}{P}\right)^{1/\gamma} \tag{23}$$

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

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S \tag{24}$$

$$= -\left(\frac{P}{K}\right)^{1/\gamma}\left(-\frac{1}{\gamma}\right)\left(\frac{K}{P}\right)^{1/\gamma}\frac{1}{P} \tag{25}$$

$$= \frac{1}{P\gamma} = \frac{1}{P}\frac{f}{(f+2)} \tag{26}$$

which is the same as 21, so equation 15 checks out for an ideal gas.

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