

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

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

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

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

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

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

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

Substituting 3 into 4 we get

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

At constant temperature $dT = 0$ and we get

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

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

From the Maxwell relation from the Gibbs energy

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

Also, from the definition of the thermal expansion coefficient β

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

Combining these last two equations gives

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

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

$$dV = \beta V dT \quad (11)$$

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

$$dS = \frac{dQ}{T} \quad (12)$$

$$= C_P \frac{dT}{T} \quad (13)$$

Dividing these two relations gives

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

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

$$\kappa_T = \kappa_S + \frac{TV\beta^2}{C_P} \quad (15)$$

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

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

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

$$C_P = C_V + Nk \quad (18)$$

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

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

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

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

$$PV^\gamma = K \quad (22)$$

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

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

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

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

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

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

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