**ISOTHERMAL AND ISENTROPIC COMPRESSIBILITIES**

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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

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

\[
\kappa_S \equiv -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_S
\]

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

\[
dS = \left( \frac{\partial S}{\partial P} \right)_T dP + \left( \frac{\partial S}{\partial T} \right)_P dT
\]

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

\[
dV = \left( \frac{\partial V}{\partial P} \right)_S dP + \left( \frac{\partial V}{\partial S} \right)_P dS
\]

Substituting 3 into 4 we get

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

At constant temperature \( dT = 0 \) and we get

\[
\left( \frac{\partial V}{\partial P} \right)_T = \left( \frac{\partial V}{\partial S} \right)_P \left( \frac{\partial S}{\partial P} \right)_T + \left( \frac{\partial V}{\partial P} \right)_S
\]

\[
-V\kappa_T = \left( \frac{\partial V}{\partial S} \right)_P \left( \frac{\partial S}{\partial P} \right)_T - V\kappa_S
\]

From the Maxwell relation from the Gibbs energy
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\[
\left( \frac{\partial S}{\partial P} \right)_T = -\left( \frac{\partial V}{\partial T} \right)_P
\]  

(8)

Also, from the definition of the thermal expansion coefficient \( \beta \)

\[
\beta \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P
\]

(9)

Combining these last two equations gives

\[-V \kappa_T = -\beta V \left( \frac{\partial V}{\partial S} \right)_P - V \kappa_S
\]

(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

\[dV = \beta V \, dT \]

(11)

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

\[dS = \frac{dQ}{T} = C_P \, dT \]

(12) \quad (13)

Dividing these two relations gives

\[\left( \frac{\partial V}{\partial S} \right)_P = \frac{TV \beta}{C_P}
\]

(14)

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

\[\kappa_T = \kappa_S + \frac{TV \beta^2}{C_P}
\]

(15)

For an ideal gas, we can use this equation to work out \( \kappa_S \):
\[
\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \frac{Nk}{PV} = \frac{1}{T} \tag{16}
\]

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

\[
C_P = C_V + Nk = Nk \left( 1 + \frac{f}{2} \right) \tag{18}
\]

\[
\kappa_S = \frac{1}{P} - \frac{V}{NkT \left( 1 + \frac{f}{2} \right)} \tag{19}
\]

\[
= \frac{1}{P} \frac{f}{(f+2)} \tag{20}
\]

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

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

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

\[
= \frac{1}{P^{\gamma}} = \frac{1}{P (f+2)} \tag{26}
\]

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

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