§ 16  Relations between the Derivatives of Thermodynamic Quantities

Derivatives most often arise in connection with the following formulae, which express the differentials of the thermodynamic quantities:

\[
\frac{dS}{dT} = \frac{T}{V} \frac{dP}{dV} \quad \text{and} \quad \frac{dS}{dP} = \frac{T}{V} \frac{dT}{dV}.
\]

These can be rewritten as:

\[
\frac{\partial S}{\partial T} = -T \frac{\partial V}{\partial P} \quad \text{and} \quad \frac{\partial S}{\partial P} = T \frac{\partial V}{\partial T}.
\]

To transform these relations to different independent variables, we use the Jacobians. We write

\[
C_v = T \left( \frac{\partial S}{\partial T} \right)_T = T \frac{\partial (S, V)}{\partial (T, V)} = T \left( \frac{\partial S}{\partial T} \right)_T \frac{\partial (V, P)}{\partial (T, P)} = T \frac{\partial S/\partial T}{\partial V/\partial T} \frac{\partial V/\partial P}{\partial T/\partial P}.
\]

Substituting (16.4), we obtain the required formula:

\[
C_p - C_v = -T \left( \frac{\partial V}{\partial T} \right)_T \frac{\partial V}{\partial P}.
\]

Similarly, transforming \( C_p = T \left( \frac{\partial S}{\partial T} \right)_p \) to the variables \( T, V \), we can derive the formula:

\[
C_p - C_v = -T \left( \frac{\partial P}{\partial T} \right)_T \frac{\partial P}{\partial V}.
\]

The derivative \( \frac{\partial P}{\partial V} \) is negative: in an isothermal expansion of a body, its pressure always decreases. This will be rigorously proved in § 21. It therefore follows from (16.10) that for all bodies

\[
C_p > C_v.
\]

† The Jacobian \( \frac{\partial (u, v)}{\partial (x, y)} \) is defined as the determinant

\[
\frac{\partial (u, v)}{\partial (x, y)} = \left| \begin{array}{cc} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{array} \right|.
\]

It clearly has the following properties:

\[
\frac{\partial (v, u)}{\partial (x, y)} = -\frac{\partial (u, v)}{\partial (x, y)},
\]

\[
\frac{\partial (u, y)}{\partial (x, y)} = \left( \frac{\partial u}{\partial x} \right)_y.
\]

The following relations also hold:

\[
\frac{\partial (u, v)}{\partial (x, y)} = \frac{\partial (u, v)}{\partial (x, y)} \frac{\partial (t, s)}{\partial (x, y)},
\]

\[
\frac{d}{dt} \frac{\partial (u, v)}{\partial (x, y)} = \frac{\partial (du/dt, v)}{\partial (x, y)} + \frac{\partial (u, dv/dt)}{\partial (x, y)}.
\]
In adiabatic expansion (or contraction) of a body its entropy remains constant. The relation between the temperature, volume and pressure of the body in an adiabatic process is therefore determined by various derivatives taken at constant entropy. We shall derive formulae whereby these derivatives may be calculated from the equation of state of the body and its specific heat.

For the derivative of the temperature with respect to volume we have, changing to independent variables \( V, T \),

\[
\left( \frac{\partial T}{\partial V} \right)_S = \frac{\partial (T, S)}{\partial (V, S)} = \frac{\partial (T, S)}{\partial (V, T)} = -\left( \frac{\partial S/\partial V}{\partial S/\partial T} \right)_V = -\frac{T}{C_v} \left( \frac{\partial S}{\partial V} \right)_T,
\]

or, substituting (16.3),

\[
\left( \frac{\partial T}{\partial V} \right)_S = -\frac{T}{C_v} \left( \frac{\partial P}{\partial T} \right)_V.
\]  

(16.12)

Similarly we find

\[
\left( \frac{\partial T}{\partial P} \right)_S = -\frac{T}{C_p} \left( \frac{\partial V}{\partial T} \right)_P.
\]  

(16.13)

These formulae show that, according as the thermal expansion coefficient \((\partial V/\partial T)_P\) is positive or negative, the temperature of the body falls or rises in an adiabatic expansion.†

Let us next calculate the adiabatic compressibility \((\partial V/\partial P)_S\) of the body, writing

\[
\left( \frac{\partial V}{\partial P} \right)_S = \frac{\partial (V, S)}{\partial (P, S)} = \frac{\partial (V, S)/\partial (V, T)}{\partial (P, S)/\partial (P, T)} \cdot \frac{\partial (V, T)}{\partial (P, T)} = \left( \frac{\partial S/\partial T}{\partial S/\partial P} \right)_P \cdot \left( \frac{\partial V}{\partial P} \right)_T
\]

or

\[
\left( \frac{\partial V}{\partial P} \right)_S = \frac{C_v}{C_p} \left( \frac{\partial V}{\partial P} \right)_T.
\]  

(16.14)

The inequality \( C_p > C_v \) therefore implies that the adiabatic compressibility is always smaller in absolute value than the isothermal compressibility.

†In § 21 it will be shown rigorously that \( C_v \) is always positive, and therefore so is \( C_p \).