If we choose \( V \) and \( T \) as the independent variables, we can express the differential of \( E \) as a function of \( V \) and \( T \). We also have the differential relationship \( dE = TdS - PdV \). These expressions for \( dE \) must be equal:

\[
dE = \left( \frac{\partial E}{\partial V} \right)_T dV + \left( \frac{\partial E}{\partial T} \right)_V dT = TdS + PdV
\]

Rearranging, we find a total differential for \( dS \) with \( V \) and \( T \) as the independent variables:

\[
dS = \frac{1}{T} \left[ \left( \frac{\partial E}{\partial T} \right)_V dT + \left( \frac{\partial E}{\partial V} \right)_T + P \right] dV
\]

From the coefficient of \( dT \), we have

\[
\left( \frac{\partial S}{\partial T} \right)_V = \frac{1}{T} \left( \frac{\partial E}{\partial T} \right)_V = \frac{C_V}{T}
\]

where we use the definition \( \left( \frac{\partial E}{\partial T} \right)_V = C_V \). (When we write “\( (C_V) \),” we usually think of it as a property of a pure substance. The relationship above is valid for any reversible system. When we are describing a system that is not a pure substance, \( (C_V) \) is just an abbreviation for \( \left( \frac{\partial E}{\partial T} \right)_V \).) From the coefficient of \( dV \), we have

\[
\left( \frac{\partial S}{\partial V} \right)_T = \frac{1}{T} \left[ \left( \frac{\partial E}{\partial V} \right)_T + P \right] = \left( \frac{\partial P}{\partial T} \right)_V
\]

where we use the relationship \( \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \) that we find in §1. Substituting into the expression for \( dS \), we find \( dS = \frac{C_V}{T} dT + \left( \frac{\partial P}{\partial T} \right)_V dV \)

Now, from \( dE = TdS - PdV \), we have

\[
dE = C_V dT + \left[ T \left( \frac{\partial P}{\partial T} \right)_V + P \right] dV
\]

From \( H = E + PV \), we have

\[
\text{\begin{align*}
\\mathrm{d}H &= \mathrm{d}E + \mathrm{d}(PV) \\
&= \mathrm{d}E + \left( \frac{\partial (PV)}{\partial T} \right)_V dT + V \left( \frac{\partial P}{\partial T} \right)_V dV + \left( \frac{\partial P}{\partial V} \right)_T dV
\end{align*}}
\]

Of course, we already have

\[
\text{\( dA = -SdT + PdV \)}
\]

From \( G = H - TS \), by an argument that parallels the above derivation of \( dH \), we obtain

\[
\text{\( dG = \left[ V \left( \frac{\partial P}{\partial T} \right)_V + S \right] dT + V \left( \frac{\partial P}{\partial V} \right)_T dV \)}
\]

Finally, we can write \( \text{\( P = P \left( T, V \right) \) \) to find}

\[
\text{\( P = \left( \frac{\partial P}{\partial T} \right)_V + V \left( \frac{\partial P}{\partial V} \right)_T \)}
\]
\[dP = \left(\frac{\partial P}{\partial T}\right)_VdT + \left(\frac{\partial P}{\partial V}\right)_TdV\]

\((P), (T), (V), (C_V), \left(\frac{\partial P}{\partial T}\right)_V\), and \(\left(\frac{\partial P}{\partial V}\right)_T\) are all experimentally accessible for any reversible system. If we have this information for a system that undergoes a change from a state specified by \((T_1)\) and \((V_1)\) to a second state specified by \((T_2)\) and \((V_2)\), we can use these relationships to calculate \(\Delta E\), \(\Delta S\), and \(\Delta H\). To do so, we calculate the appropriate line integral along a reversible path. One such path is an isothermal reversible change, at \((T_1)\), from \((V_1)\) to \((V_2)\), followed by a constant-volume change, at \((V_2)\), from \((T_1)\) to \((T_2)\). In principle, the same procedure can used to calculate \(\Delta A\) and \(\Delta G\). However, because \((S)\) appears in the differentials \(\mathrm{d}A\) and \(\mathrm{d}G\), this requires that we first find \((S)\) as a function of \((V)\) and \((T)\).

If the system is a pure substance for which we have an equation of state, we can find \(\left(\frac{\partial P}{\partial T}\right)_V\), and \(\left(\frac{\partial P}{\partial V}\right)_T\) by straightforward differentiation. When the substance is a gas, an equation of state may be available in the literature. When the substance is a liquid or a solid, these partial derivatives can still be related to experimentally accessible quantities. The compressibility of a substance is the change in its volume that results from a change in the applied pressure, at a constant temperature. The thermal expansion of a substance is the change in its volume that results from a change in its temperature, at a constant applied pressure. It is convenient to convert measurements of these properties into intensive functions of the state of the substance by expressing the volume change as a fraction of the original volume. That is, we define the coefficient of thermal expansion:

\[\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\]

and the coefficient of isothermal compressibility:

\[\beta = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T\]

Coefficients of thermal expansion and isothermal compressibility are available in compilations of thermodynamic data for many liquids and solids. In general, both coefficients are weak functions of temperature. We have

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

and

\[\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T = \frac{\alpha}{\beta}\]

Using these coefficients, we can estimate a pressure change, for example, as a line integral of

\[dP = \left(\frac{\alpha}{\beta}\right)dT - \left(\frac{1}{\beta V}\right)dV\]