Thermodynamic state functions expressed in differential form

We have seen that the internal energy is conserved and depends on mechanical (dw) and thermal (dq) energy. Given that pressure-volume work done by the system is \( dw = -PdV \) and that the entropy change can be expressed as \( dS = dq/T \) (i.e. \( dq = TdS \)) we can express the internal energy as

\[
dU = TdS - pdV
\]

By a transformation of variables we define \( H = U + PV \) or \( dH = d(U+PV) = dU + PdV + VdP \). Therefore,

\[
dH = TdS + VdP
\]

These two expressions are known as total derivatives.
The total derivative

The total derivative permits more than one variable to change at one time. We can write the state functions $U$ and $H$ in the following form to make it clearer what the variable dependencies are:

\[
\begin{align*}
    dU &= \left( \frac{\partial U}{\partial S} \right)_V \ dS + \left( \frac{\partial U}{\partial V} \right)_S \ dV \\
    dH &= \left( \frac{\partial H}{\partial S} \right)_P \ dS + \left( \frac{\partial H}{\partial P} \right)_S \ dP
\end{align*}
\]

which implies that

\[
\begin{align*}
    T &= \left( \frac{\partial U}{\partial S} \right)_V, \quad P = - \left( \frac{\partial U}{\partial V} \right)_S \\
    T &= \left( \frac{\partial H}{\partial S} \right)_P, \quad V = \left( \frac{\partial H}{\partial P} \right)_S
\end{align*}
\]
Definition of an exact differential

In the general case we can write a total derivative as:
\[ dF = F_x \, dx + F_y \, dy \]

or
\[ dF = \left( \frac{\partial F}{\partial x} \right)_y \, dx + \left( \frac{\partial F}{\partial y} \right)_x \, dy \]

If the total derivative is an exact differential then the second derivatives of both terms in the differential are equal.
\[ F_{yx} = \frac{\partial F_x}{\partial y} = \frac{\partial F}{\partial y \partial x} = \frac{\partial F}{\partial x \partial y} = \frac{\partial F_y}{\partial x} = F_{xy} \]
Second derivatives of the internal energy function

The differential form of the internal energy is:

\[ dU = TdS - PdV \]

Using the definitions we determined above:

\[ T = \left( \frac{\partial U}{\partial S} \right)_V, \quad P = - \left( \frac{\partial U}{\partial V} \right)_S \]

The second derivatives can be written as:

\[ \frac{\partial T}{\partial V} = \frac{\partial U}{\partial V \partial S} = \frac{\partial U}{\partial S \partial V} = - \frac{\partial P}{\partial S} \]
Second derivatives of the enthalpy function

The differential form of the enthalpy is:

\[ dH = TdS + VdP \]

Using the definitions we determined above:

\[ T = \left( \frac{\partial H}{\partial S} \right)_P, \quad V = \left( \frac{\partial H}{\partial P} \right)_S \]

The second derivatives can be written as:

\[ \frac{\partial T}{\partial P} = \frac{\partial H}{\partial P} = \frac{\partial H}{\partial S} = \frac{\partial V}{\partial S} \]
Second derivatives of the Gibbs free energy function

The differential form of the Gibbs energy is:
\[ dG = VdP - SdT \]

Using the definitions we determined above:
\[ V = \left( \frac{\partial G}{\partial P} \right)_T, \quad -S = \left( \frac{\partial G}{\partial T} \right)_P \]

The second derivatives can be written as:
\[ -\frac{\partial S}{\partial P} = \frac{\partial G}{\partial P} = \frac{\partial G}{\partial T} = \frac{\partial V}{\partial T} \]
Second derivatives of the Helmholtz free energy function

The differential form of the Gibbs energy is:
\[ \text{d}A = - P \text{d}V - S \text{d}T \]

Using the definitions we determined above:
\[-P = \left( \frac{\partial A}{\partial V} \right)_T, \quad -S = \left( \frac{\partial A}{\partial T} \right)_V \]

The second derivatives can be written as:
\[-\frac{\partial P}{\partial T} = \frac{\partial A}{\partial T \partial V} = \frac{\partial A}{\partial V \partial T} = - \frac{\partial S}{\partial V} \]
Summary of Maxwell Relations

For each of the four state functions $U$, $H$, $A$ and $G$ we can derive a corresponding Maxwell relation:

$U$
\[ \frac{\partial T}{\partial V} = - \frac{\partial P}{\partial S} \]

$H$
\[ \frac{\partial T}{\partial P} = \frac{\partial V}{\partial S} \]

$A$
\[ \frac{\partial P}{\partial T} = \frac{\partial S}{\partial V} \]

$G$
\[ - \frac{\partial S}{\partial P} = \frac{\partial V}{\partial T} \]