With \((U), \(A), \(H)\) and \((G)\) in hand we have potentials as a functions of whichever variable pair we want: \((S)\) and \((V)\), to \((T)\) and \((P)\). Additional Legendre transforms will provide us with further potentials in case we have other variables (such as surface area \((A)\), length \((L)\), magnetic moment \((M)\), etc.).

Thermodynamic problems always involve computing a variable of interest. It may be a derivative if it is an intensive variable, or even a second derivative (higher derivatives are rarely of interest).

**Example**

1st order ones like

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

or 2nd order ones like

\[
\left( \frac{\partial^2 G}{\partial P^2} \right)_T = \left( \frac{\partial V}{\partial P} \right)_T = \kappa V
\]

The solution procedure is thus:

1. Select the derivative or variable to be computed;
2. Select the potential representation that makes it easiest, or corresponds to variables you already have in hand.
3. Manipulate the thermodynamic derivative you know to get the one you want.

Easy as 1-2-3! We now turn to two methods to manipulate the thermodynamic derivations:

### 6.1 Tool 1: Maxwell relations

This tool is useful if two variables are NOT conjugate (e.g. \((T)\) and \((V)\) as opposed to \((T)\) and \((S)\))

If \((z = z(x,y))\), then its total differential is:

\[
\left( \frac{\partial^2 z}{\partial x \partial y} \right) = \left( \frac{\partial^2 z}{\partial y \partial x} \right)
\]

Maxwell’s relations must hold true if \((z)\) is a *state function*, as we saw in [chapter 1](#). They basically state that the cross-second derivatives of a function must be identical.
Example 6.1

\[ dG = -SdT + VdP + \mu dn \]

\[ - \left( \frac{\partial S}{\partial P} \right)_{T,n} = - \left( \frac{\partial V}{\partial T} \right)_{P,n} = \kappa V \]

or

\[ - \left( \frac{\partial V}{\partial n} \right)_{P,T} = - \left( \frac{\partial \mu}{\partial P} \right)_{n,T} \]

All four of the quantities in parenthesis are second derivatives of \( G \). We can verify the second line above for an ideal gas:

\[ - \left( \frac{\partial \mu}{\partial P} \right)_{n,T} = \frac{\partial}{\partial P} RT\ln P = \frac{RT}{P} \]

and

\[ - \left( \frac{\partial V}{\partial n} \right)_{P,T} = \frac{\partial}{\partial n} \frac{nRT}{P} = \frac{RT}{P} \]

Note: As discussed in chapter 7, only three second derivatives not involving \( n_i \) are independent; many sets can be chosen; the conventional one is \( \{\alpha, \kappa, c_P\} \), all defined at constant \( T \) or \( P \) (Gibbs ensemble). You can preview them at the beginning of chapter 7.

6.2 Tool 2: Jacobi Determinants

To reduce thermodynamic formulas to a minimal number of derivatives (e.g. \( \{\alpha, \kappa, c_P\} \)), the Jacobi determinants can be used in addition to the Maxwell relations. The idea is that you can reduce ANY derivative or variable you want to functions of \( T, P, n \) (if working in the Gibbs ensemble, other combinations otherwise) and second derivatives \( \{\alpha, \kappa, c_P\} \) (others in different ensembles).

The Jacobi determinant is defined as

\[ \frac{\partial (x,y,...z)}{\partial (u,v,...w)} \equiv \text{det} \begin{vmatrix} \left( \frac{\partial x}{\partial u} \right) & \left( \frac{\partial x}{\partial v} \right) & \left( \frac{\partial x}{\partial w} \right) \\ \left( \frac{\partial y}{\partial u} \right) & \left( \frac{\partial y}{\partial v} \right) & \left( \frac{\partial y}{\partial w} \right) \\ \left( \frac{\partial z}{\partial u} \right) & \left( \frac{\partial z}{\partial v} \right) & \left( \frac{\partial z}{\partial w} \right) \end{vmatrix} \]

Jacobians are useful for any variables transformation \( ((u, v, ... w) \rightarrow (x, y, ... z)) \). Any thermodynamic derivative can be expressed as follows:

\[ \left( \frac{\partial x}{\partial u} \right)_{v...w} = \frac{\partial (x,y,...z)}{\partial (u,v,...w)} \frac{\partial (x,y,...z)}{\partial (u,v,...w)} \]

because
in the above determinant will leave only the desired derivative when the determinant is multiplied out. The derivatives can then be manipulated by using the *Jacobian identities*:

i)

\[
\dfrac{\partial (x,y,...z)}{\partial (u,v,...w)} = -\dfrac{\partial (y,x,...z)}{\partial (u,v,...w)} = -\dfrac{\partial (x,y,...z)}{\partial (v,u,...w)} \]

via the properties of row or column permutation of determinants.

ii)

\[
\dfrac{\partial (x,y,...z)}{\partial (u,v,...w)} = \dfrac{\partial (y,x,...z)}{\partial (r,s,...t)} \cdot \dfrac{\partial (r,s,...t)}{\partial (v,u,...w)} \]

For example:

iii)

\[
\dfrac{\partial (x,y,...z)}{\partial (u,v,...w)} = \dfrac{1}{\dfrac{\partial (u,v,...w)}{\partial (x,y,...z)}} \]

**Proof**

\[
\det(M^{-1}) = \dfrac{1}{\det(M)} \]

This concludes all the formal thermodynamic tools: From \(\Delta S > 0\) (from Postulate 2), to the *Euler formula*, *Legendre Transforms*, and finally Maxwell relations and Jacobians, you have all the problem-solving tools thermodynamics has to offer to tackle equilibrium problems.

Armed with the Maxwell and Jacobian relations, we can reduce any expression to \(\alpha\), \(\kappa\), and \(c_p\) (plus concentration or other derivatives, depending on the extensive variables of the system). Let us do a few examples:

### 6.3 Applications

**Example 6.1: Heat Capacity at Constant Volume**

Evaluated the heat capacity at constant volume in terms of heat capacity at constant pressure.

**SOLUTION**

\[
c_b \equiv \left(\dfrac{dq}{dT}\right)_V = \dfrac{T}{n}\left(\dfrac{\partial S}{\partial T}\right)_V \tag{1}\]

Step 1: is there a Maxwell relation? **NO**: \(\{S\} \& \{T\}\) are conjugate variables, so use a Jacobian
\[
\dfrac{T}{n} \dfrac{\partial (S,V)}{\partial (T,V)} \quad \tag{2}
\]

Step 2: we want \( P \) held constant in the Jacobian, not \( V \), so split the Jacobian by chain rule

\[
\dfrac{T}{n} \dfrac{\partial (S,V)}{\partial (T,P)} \dfrac{\partial (T,P)}{\partial (T,V)} \quad \tag{3}
\]

Step 3: Flip columns in the second Jacobian and evaluate \( (\partial P/\partial V)_T \), the isothermal compressibility \( \kappa \)

\[
\dfrac{n \kappa}{T} = \dfrac{\partial (S,V)}{\partial (T,P)} \quad \tag{4}
\]

Step 4: Can we use Maxwell or Jacobians? \textbf{NO:} time to multiply out the determinant

\[
= -\dfrac{T}{n V \kappa} \left\{ \left( \dfrac{\partial S}{\partial T} \right)_P \left( \dfrac{\partial V}{\partial P} \right)_T - \left( \dfrac{\partial S}{\partial P} \right)_T \left( \dfrac{\partial V}{\partial T} \right)_P \right\} \quad \tag{5}
\]

Step 5: We know three of the derivatives in terms of second derivatives of the Gibbs free energy. The missing one, \( (\partial S/\partial P)_T = ? ) \) can be obtained using Maxwell: \( \kappa = (\partial P/\partial V)_T \), just the isobaric expansion coefficient \( \alpha \).

\[
\dfrac{n C_p}{T} \left( \dfrac{V}{\kappa} \right) - (V \alpha) \quad \tag{6}
\]

Step 6: Collect everything and note that \( \alpha, (\kappa, n) \) and \( \kappa \) are all positive, as is \( \alpha^2 \), so \( c_v \) must always be smaller than \( c_p \). This should make intuitive sense: if I keep a system at constant pressure and put heat in it, it will also expand, ‘losing’ some of the heat as work. Thus the temperature will not go up as much, so the heat capacity is bigger at constant pressure.

\[
= c_p -\dfrac{T \alpha^2}{n \kappa} \quad \tag{7}
\]

\[
\Rightarrow c_p \gt c_v
\]

Example 6.2: Change in Enthalpy at Constant P

Calculate the change in enthalpy at constant pressure.

\[
\left\{ \left( \dfrac{\partial H}{\partial T} \right)_P, n \right\} = \left\{ \left( \dfrac{\partial H}{\partial S} \right)_P, n \right\} \left( \dfrac{\partial S}{\partial T} \right)_P = T \left( \dfrac{n C_p}{T} \right) = nc_p
\]

Thus \( dH = n c_v \, dT \). We derived this earlier by waving hands and using \( dq_{rev} \), but here it is, formally.

Example 6.3 Isentropic Quasistatic Expansion
In an isentropic quasistatic expansion, \( S = \text{constant} \), so \( dq_{\text{rev}}/T - dS = 0 \). Do the homework problem before you check out the solution below!

This describes the pressure-temperature relationship in a molecular beam, where no heat can flow into the expanding gas, so its temperature must drop as the pressure drops. What happens is that at the nozzle of the molecular beam, collisions preferentially eject particles forward, preserving their average kinetic energy, but making a stream of particles with a narrower relative velocity distribution. The relevant derivative is \( \frac{\partial T}{\partial P} \), which looks a bit odd at first, but we are fully equipped to handle derivatives at constant entropy:

\[
0 = dS = \frac{dq_{\text{rev}}}{T}
\]

\[
\Rightarrow \frac{\partial(T,S)}{\partial(P,S)} \frac{\partial(T,S)}{\partial(P,T)} \frac{\partial(P,T)}{\partial(P,S)} = -\frac{\partial(S,T)}{\partial(P,S)} \cdot \frac{1}{\frac{\partial(S,P)}{\partial(T,P)}} = -\frac{\left(\frac{\partial S}{\partial P}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_P}
\]

For the numerator, \( (\frac{\partial S}{\partial P})_T = (\frac{\partial V}{\partial T})_P = \alpha V \) by the Maxwell relations.

Note that just because \( S \) is constrained to be held constant in \( (\frac{\partial T}{\partial P})_S \) does not mean that \( (\frac{\partial S}{\partial P})_T = 0 \)!

For the denominator

\[
\frac{\partial(T,S)}{\partial(P,S)} \frac{\partial(T,S)}{\partial(P,T)} = \frac{\partial(S,T)}{\partial(P,S)} \cdot \frac{1}{\frac{\partial(S,P)}{\partial(T,P)}}
\]

For an ideal monatomic gas, \( \alpha = \frac{\partial V}{\partial T} = \frac{\partial nR}{\partial T} \), and \( c_p = \frac{\partial (5/2) R}{\partial T} \) so we can write explicitly

\[
\frac{dT}{T} = \frac{2}{5} \frac{dP}{P}
\]

or

\[
\left(\frac{T}{T_0}\right) = \left(\frac{P}{P_0}\right)^{\frac{2}{5}}
\]

after integrating. The temperature drops in a molecular beam, but not as dramatically as the pressure.

**Example 6.4: Heat Capacity in terms of Energy**

\[
c_v = \left(\frac{dq}{dT}\right)_V = \frac{T}{n} \left(\frac{\partial S}{\partial T}\right)_V
\]
with \( T > 0 \) and \( n > 0 \)

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

\[
c_v = \frac{1}{n} \left( \frac{\partial U}{\partial T} \right)_V = \frac{T}{n} \left( \frac{\partial S}{\partial T} \right)_V
\]

Again, we showed this before by invoking \( dq_{\text{rev}} \) when discussing Legendre Transforms from energy to enthalpy. Examples 6.1 and 6.3 are just the formal way of deriving it using Maxwell’s relations and Jacobians.

**Contributors**

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