Chapter 16
More on Property Relations

16.1 Measurability of Properties

Some properties are easy to measure, and thus quite intuitive, e.g., pressure p, temperature T and specific volume v. Accordingly, the thermal equation of state, $p(T,v)$ can be measured with relative ease. Other properties cannot be measured directly, for instance internal energy u or enthalpy h, which must be determined by means of applying the first law to a calorimeter, or entropy s, which must be determined from other properties by integration of the Gibbs equation.

The Gibbs equation

$$Tds = du + pdv \tag{16.1}$$

gives a differential relation between properties for any simple substance. Its analysis with the tools of multivariable calculus, as presented below, shows that specific internal energy $u = U/m$, specific enthalpy $h = H/m$, specific Helmholtz free energy $f = u - Ts$, and specific Gibbs free energy $g = h - Ts$ are potentials when considered as functions of particular variables. The evaluation of the potentials leads to a rich variety of relations between thermodynamic properties which will be derived and explored in this chapter. In particular, these relate properties that are more difficult, or even impossible, to measure to those that are more easy to measure, and thus reduce the necessary measurements to determine data for all properties.

Later, in Chapter 17, it will be seen that the thermodynamic potentials play an important role in finding the equilibrium states of a system.

16.2 Thermodynamic Potentials and Maxwell Relations

We rewrite the Gibbs equation as

$$du = Tds - pdv\ . \tag{16.2}$$

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This equation suggests to consider the internal energy u as a function of entropy s and volume v, that is $u\,(s,v)$. Its exact differential (u is a state function) is given by

$$du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv \,, \tag{16.3}$$

and by comparison with (16.2) we identify

$$T = \left(\frac{\partial u}{\partial s}\right)_v \quad , \quad -p = \left(\frac{\partial u}{\partial v}\right)_s \,. \tag{16.4}$$

Thus, the internal energy $u\,(s,v)$ is a potential, in the sense that temperature $T\,(s,v)$ and pressure $p\,(s,v)$ are obtained from derivatives of u.

The order of second derivatives can be exchanged,

$$\frac{\partial^2 u}{\partial v \partial s} = \frac{\partial^2 u}{\partial s \partial v} \,, \tag{16.5}$$

and since u is a potential for T and p, we find a relation between the derivatives of T and p, one of the so-called Maxwell relations,

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v \,. \tag{16.6}$$

For the novice, expressions like (16.6) seem to be just mathematical symbols. However, all expressions have a clear meaning which derives from the properties they entail. For instance, the expression $\left(\frac{\partial T}{\partial v}\right)_s$ gives the change of temperature with volume at constant entropy. It can be measured, in principle, by varying the volume of the system by a small amount dv while the entropy s stays constant, and measuring the associated change in temperature dT. Similarly, the expression $\left(\frac{\partial p}{\partial s}\right)_v$ describes the change of pressure with entropy at constant volume. It can be measured, in principle, in a system at constant volume v by varying the entropy by ds and recording the associated pressure change dp. Similar interpretations apply to the expressions in (16.4).

The above partial derivatives are, in fact, not accessible to measurements since one of the variables is entropy: since there is no direct measurement of entropy, it is very difficult, if not impossible, to conduct an experiment in which entropy is changed by a given amount ds, or fixed at a given value s.[1]

To find more relations of the same kind, we use that $-pdv = -d\,(pv) + vdp$, which leads to a shift in variables from v to p, a so-called Legendre transform

[1] Earlier we learned that an adiabatic and reversible process is isentropic. Thus, a process at constant entropy s can be achieved in a very slow experiment in an isolated container. However, the actual value of entropy for the given experiment cannot be determined through measurement.

(Adrien-Marie Legendre, 1752-1833). With this, the Gibbs equation (16.2) becomes $du = Tds + vdp - d(pv)$, and by introducing enthalpy as

$$h = u + pv \ , \tag{16.7}$$

the Gibbs equation assumes the alternative form

$$dh = Tds + vdp \ . \tag{16.8}$$

This equation points to considering enthalpy h as a function of entropy s and pressure p, where now $h(s,p)$ is a potential, with

$$T = \left(\frac{\partial h}{\partial s}\right)_p \quad , \quad v = \left(\frac{\partial h}{\partial p}\right)_s \ , \tag{16.9}$$
$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p \ .$$

The last equation is the Maxwell equation for this potential, it results from exchanging the order of derivatives, $\frac{\partial^2 h}{\partial p \partial s} = \frac{\partial^2 h}{\partial s \partial p}$. Again all partial derivatives contain the entropy s as one of the variables, and therefore they are not accessible to measurements.

Similarly, we can apply a Legendre transform to the term $Tds = d(Ts) - sdT$ in the Gibbs equation. This transformation exchanges the variable s, which cannot be measured directly, by the variable T, which can be measured. As a result, we find new potentials, the free energies.

The Helmholtz free energy is defined as

$$f = u - Ts \ , \tag{16.10}$$

and with this the Gibbs equation can be written in the alternative form

$$df = -sdT - pdv \ .$$

We recognize that $f(T,v)$ is a potential, with

$$-s = \left(\frac{\partial f}{\partial T}\right)_v \quad , \quad -p = \left(\frac{\partial f}{\partial v}\right)_T \ , \tag{16.11}$$
$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \ .$$

The last equation is the Maxwell equation for this potential, it results from exchanging the order of derivatives, $\frac{\partial^2 f}{\partial v \partial T} = \frac{\partial^2 f}{\partial T \partial v}$. Most remarkably, the Maxwell relation $(16.11)_3$ contains the expression $\left(\frac{\partial p}{\partial T}\right)_v$, which describes the change of pressure p with temperature T in an experiment at constant volume v. Since p, T and v can be measured, this expression can be found experimentally. In fact, measurement of $\{p, T, v\}$ gives the thermal equation of state $p(T, v)$, and we can say that $\left(\frac{\partial p}{\partial T}\right)_v$ can be determined from the thermal equation of state. The other expression, $\left(\frac{\partial s}{\partial v}\right)_T$, cannot be measured by itself, since it contains entropy s. Hence, with the Maxwell relation the expression $\left(\frac{\partial s}{\partial v}\right)_T$ can be measured through measurement of the thermal equation of state.

The Gibbs free energy is defined as

$$g = h - Ts = f + pv \ , \tag{16.12}$$

and with another Legendre transform, the Gibbs equation becomes

$$dg = -sdT + vdp \ .$$

We recognize that $g(T, p)$ is a potential, with

$$-s = \left(\frac{\partial g}{\partial T}\right)_p \quad , \quad v = \left(\frac{\partial g}{\partial p}\right)_T \ , \tag{16.13}$$

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \ .$$

The last equation is the Maxwell equation for this potential, it results from exchanging the order of derivatives, $\frac{\partial^2 g}{\partial p \partial T} = \frac{\partial^2 g}{\partial T \partial p}$. Also this Maxwell relation contains one expression that can be determined from the thermal equation of state, namely $\left(\frac{\partial v}{\partial T}\right)_p$, relating it to an expression that is not accessible to direct measurement, namely $\left(\frac{\partial s}{\partial p}\right)_T$. The usefulness of the above differential relations, in particular of those that involve expressions that can be measured, will become evident in the subsequent sections.

It is important to note that the thermodynamic properties u, h, f, g are only potentials when considered as functions of the given variables. That is only $u(s, v)$, $h(s, p)$, $f(T, v)$, $g(T, p)$ are potentials! One can use property relations to change the variables, for instance with the thermal equation of state $p(T, v)$ one obtains $g(T, p) = g(T, p(T, v)) = g(T, v)$—however, as function of T and v the Gibbs free energy is *not* a potential.

16.3 Two Useful Relations

Gibbs equation and Maxwell relations can be used to obtain additional relations between properties which will form the center of the following section on measurement of thermodynamic properties. To proceed, we consider energy and entropy in the Gibbs equation (16.2) as functions of temperature and volume, $u(T, v)$, $s(T, v)$, and evaluate their differentials as

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv \quad , \quad ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv \; . \quad (16.14)$$

After some reordering, the Gibbs equation (16.2) yields

$$\left[\left(\frac{\partial u}{\partial T}\right)_v - T\left(\frac{\partial s}{\partial T}\right)_v\right] dT + \left[\left(\frac{\partial u}{\partial v}\right)_T - T\left(\frac{\partial s}{\partial v}\right)_T + p\right] dv = 0 \; . \quad (16.15)$$

Two properties can always be controlled independently, that is in the above dT and dv must be independent. This implies that their factors, in square brackets, must vanish,

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - p \quad , \quad \left(\frac{\partial u}{\partial T}\right)_v = T\left(\frac{\partial s}{\partial T}\right)_v \; . \quad (16.16)$$

A faster approach to the first relation is to take the partial derivative of the Gibbs equation (16.2) with respect to v while keeping T constant. Similarly the second relation follows from taking the partial derivative of the Gibbs equation (16.2) with respect to T while keeping v constant.

With the Maxwell relation $(16.11)_3$ to replace the entropy derivative $\left(\frac{\partial s}{\partial v}\right)_T$ in $(16.16)_1$, we find an equation for the volume dependence of internal energy that is entirely determined by the thermal equation of state $p\,(T, v)$,

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p \; . \quad (16.17)$$

Since internal energy cannot be measured directly, the left hand side cannot be determined experimentally. However, the right hand side is determined by the thermal equation of state, $p\,(T, v)$, which is easy to measure. The equation states that the volume dependence of the internal energy is known from measurement of the thermal equation of state.

For instance for the ideal gas $p\,(T, v) = RT/v$ and thus $\left(\frac{\partial u}{\partial v}\right)_T = 0$— the internal energy of the ideal gas is independent of volume, and therefore depends only on temperature, $u = u\,(T)$. While we have used this from the beginning as an experimental fact, we see here that it is a direct consequence of the Gibbs equation and the thermal equation of state.

To obtain a similar relation for enthalpy, we take the partial derivative of the Gibbs equation $(16.9)_1$ with respect to p while keeping T constant, to obtain

$$\left(\frac{\partial h}{\partial p}\right)_T = T\left(\frac{\partial s}{\partial p}\right)_T + v \; . \quad (16.18)$$

With the Maxwell relation $(16.13)_3$ to replace the entropy derivative $\left(\frac{\partial s}{\partial p}\right)_T$, this gives an equation for the pressure dependence of enthalpy, which is entirely determined by the thermal equation of state $p\,(T, v)$, or rather $v\,(T, p)$,

$$\left(\frac{\partial h}{\partial p}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_p + v\,. \tag{16.19}$$

For instance for the ideal gas $v\,(T,p) = RT/p$ and thus $\left(\frac{\partial h}{\partial p}\right)_T = 0$—the enthalpy of the ideal gas is independent of pressure, and depends only on temperature, $h = h\,(T)$.

16.4 Relation between Specific Heats

Our first use of (16.17) is to derive a relation between the specific heats at constant volume and constant pressure,

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v \quad \text{and} \quad c_p = \left(\frac{\partial h}{\partial T}\right)_p\,. \tag{16.20}$$

It will be seen that, as long as the thermal equation of state is known, it suffices to measure one of the specific heats, the other can then be determined from the relation to be derived.

We start with the first law for reversible processes in differential form, $du = \delta q - pdv$, and insert $u\,(T,v)$, so that with the above definition of c_v

$$\delta q = du + pdv = c_v dT + \left[\left(\frac{\partial u}{\partial v}\right)_T + p\right] dv\,. \tag{16.21}$$

With the just found relation (16.17) this simplifies to

$$\delta q = c_v dT + T\left(\frac{\partial p}{\partial T}\right)_v dv\,. \tag{16.22}$$

For a constant volume process we have $dv = 0$ and thus $\delta q = c_v dT$ which relates the specific heat c_v to the heat that must be added in an isochoric process to raise the temperature by dT; in fact this is the definition of c_v as a measurable quantity. Measurement of the specific heat $c_v\,(T,v)$ is done in calorimeters, where a substance in a rigid container ($dv = 0$) originally at temperature T is carefully heated by a known amount δq, e.g., by means of a electrical resistor, and the corresponding temperature change dT is recorded. Great care must be taken to control heat leaks, so that the amount of heat added to the material is known as accurately as possible.

To introduce the specific heat at constant pressure, c_p, we proceed as follows: In the last equation, we consider volume v as function of T and p by means of the thermal equation of state $v\,(T,p)$, so that $dv = \left(\frac{\partial v}{\partial T}\right)_p dT + \left(\frac{\partial v}{\partial p}\right)_T dp$, to obtain

$$\delta q = \left[c_v + T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_p \right] dT + T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial p} \right)_T dp \, . \tag{16.23}$$

On the other hand, Legendre transform in (16.21) gives, with (16.19),

$$\delta q = dh - vdp = c_p dT + \left[\left(\frac{\partial h}{\partial p} \right)_T - v \right] dp = c_p dT - T \left(\frac{\partial v}{\partial T} \right)_p dp \, . \tag{16.24}$$

By comparison we find from the last two equations

$$c_v + T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_p = c_p \quad \text{and} \quad \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial p} \right)_T = - \left(\frac{\partial v}{\partial T} \right)_p \, . \tag{16.25}$$

Thus, the two specific heats are related as

$$c_p - c_v = T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_p = -T \left(\frac{\partial p}{\partial v} \right)_T \left[\left(\frac{\partial v}{\partial T} \right)_p \right]^2 \, . \tag{16.26}$$

The right hand side is known when the thermal equation of state, $p(T, v)$, is known. Thus, if one of the specific heats and the thermal equation of state are measured, the other specific heat is known. It is easy to show from the above that for the ideal gas $c_p - c_v = R$.

Finally, we note that straightforward application of the Gibbs equation in (16.20) yields the equivalent expressions for the specific heats

$$c_v = T \left(\frac{\partial s}{\partial T} \right)_v \quad \text{and} \quad c_p = T \left(\frac{\partial s}{\partial T} \right)_p \, , \tag{16.27}$$

see the above derivation of (16.16) for details.

16.5 Measurement of Properties

Only few thermodynamic properties can be measured easily, namely temperature T, pressure p, and volume v. These are related by the thermal equation of state $p(T, v)$ which is therefore relatively easy to measure.

The specific heats (16.20) can be measured in careful measurements where, because of (16.26), it suffices to measure either c_v or c_p. These calorimetric measurements employ the first law, where the change in temperature in response to the heat added to the system is measured.

Other important quantities, however, e.g., u, h, f, g, s, cannot be measured directly. In the following we shall study how they can be related to measurable quantities, i.e., T, p, v, and c_v by means of the Gibbs equation and the differential relations derived above.

We first consider the measurement of internal energy. The differential of $u(T,v)$ is

$$du = c_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv\,. \tag{16.28}$$

Therefore, the internal energy $u(T,v)$ can be determined by integration when c_v and $\left(\frac{\partial u}{\partial v}\right)_T$ are known from measurements. By (16.17) the term $\left(\frac{\partial u}{\partial v}\right)_T$ is known through measurement of the thermal equation of state, and we can write

$$du = c_v dT + \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] dv\,. \tag{16.29}$$

Thus, only the specific heat $c_v(T,v)$ must be measured when the thermal equation of state $p(T,v)$ is already known.

To determine what measurements must be taken to determine the specific heat $c_v(T,v) = \left(\frac{\partial u}{\partial T}\right)_v$, we consider its differential,

$$dc_v = \left(\frac{\partial c_v}{\partial T}\right)_v dT + \left(\frac{\partial c_v}{\partial v}\right)_T dv\,. \tag{16.30}$$

From the definition of c_v follows, with (16.17),

$$\begin{aligned}\left(\frac{\partial c_v}{\partial v}\right)_T &= \frac{\partial^2 u}{\partial v \partial T} = \frac{\partial^2 u}{\partial T \partial v} = \frac{\partial}{\partial T}\left(\frac{\partial u}{\partial v}\right)_T \\ &= \frac{\partial}{\partial T}\left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v\,.\end{aligned} \tag{16.31}$$

Thus, the volume dependence of c_v follows from measurement of the thermal equation of state.

Accordingly, in order to determine the specific heat $c_v(T,v)$ for all T and v it is sufficient to measure the thermal equation of state $p(T,v)$ for all (T,v) and the specific heat $c_v(T,v_0)$ for all temperatures T but only one volume v_0. Then, $c_v(T,v)$ follows from integration of (16.30). Finally, integration of (16.28) gives the internal energy $u(T,v)$.

Integration is performed from a reference state (T_0,v_0) to the actual state (T,v). Since internal energy is a point function, its differential is exact, and the integration is independent of the path chosen. The easiest integration is in two steps, first at constant volume v_0 from (T_0,v_0) to (T,v_0), then at constant temperature T from (T,v_0) to (T,v). The integration results in

$$\begin{aligned}&u(T,v) - u(T_0,v_0) = \\ &= \int_{T_0}^{T} c_v(T',v_0)\,dT' + \int_{v_0}^{v}\left[T\left(\frac{\partial p}{\partial T}\right)_{v'} - p(T,v')\right] dv' + \sum_i \Delta u_i\,.\end{aligned} \tag{16.32}$$

The internal energy can only be determined apart from a reference value $u(T_0, v_0)$. As long as no chemical reactions occur, the energy constant $u(T_0, v_0)$ can be arbitrarily chosen; see Chapter 23 on chemical reactions for additional discussion. When phase changes are involved, the respective energies Δu_i have to be added.

Enthalpy can be obtained from integration of its differential

$$dh = c_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp = c_p dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp\,, \qquad (16.33)$$

where (16.19) was used. Here, integration is performed from (T_0, p_0) to (T, p). When we integrate in two steps, first at constant pressure p_0 from (T_0, p_0) to (T, p_0), then at constant temperature T from (T, p_0) to (T, p), the integration gives

$$\begin{aligned} &h(T,p) - h(T_0, p_0) = \\ &= \int_{T_0}^{T} c_p(T', p_0)\, dT' + \int_{p_0}^{p} \left[v(T, p') - T\left(\frac{\partial v}{\partial T}\right)_{p'}\right] dp' + \sum_i \Delta h_i\,. \qquad (16.34) \end{aligned}$$

Here we have explicitly introduced the heats of phase change Δh_i which must be added whenever the line of integration crosses a saturation curve in the p-T-diagram. The reference enthalpy $h(T_0, p_0)$ can be chosen arbitrarily as long as no chemical reactions occur. In case of chemical reactions, it should be chosen as the enthalpy of formation, see the discussion in the chapter on chemical reactions.

Entropy $s(T, p)$ follows by integration of the Gibbs equation, e.g., in the form

$$ds = \frac{1}{T} dh - \frac{v}{T} dp = \frac{c_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_p dp\,,$$

as

$$s(T,p) - s(T_0, p_0) = \int_{T_0}^{T} \frac{c_p(T', p_0)}{T'} dT' - \int_{p_0}^{p} \left(\frac{\partial v}{\partial T}\right)_{p'} dp' + \sum_i \frac{\Delta h_i}{T_i}\,; \qquad (16.35)$$

Also entropy can be determined only apart from a reference value $s(T_0, v_0)$ which only plays a role when chemical reactions occur; see Chapter 23. When the line of integration crosses saturation lines in the p-T-diagram, the corresponding entropy changes $\Delta s_i = \frac{\Delta h_i}{T_i}$ must be included. This can be seen as follows: At an equilibrium phase interface, temperature T and (saturation) pressure $p_{\mathrm{sat}}(T)$ are continuous. Integration of the Gibbs equation $Tds = dh - vdp$ across the phase interface yields $T\Delta s = \Delta h$.

For the ideal gas, where $\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p}$ and the specific heat depends on T only, enthalpy and entropy assume the familiar forms (with suitable choice of integration constants)

$$h(T) = \int_{T_0}^{T} c_p(T')\,dT' \,, \tag{16.36}$$

$$s(T,p) = s^0(T) - R\ln\frac{p}{p_0} \quad \text{with} \quad s^0(T) = \int_{T_0}^{T} \frac{c_p(T',p_0)}{T'}dT' \,.$$

After u, h and s are determined, Helmholtz free energy f and Gibbs free energy g simply follow by means of their definitions (16.10, 16.12). Thus the measurement of *all* thermodynamic quantities requires only the measurement of the thermal equation of state $p(T,v)$ for all (T,v) and the measurement of the specific heat at constant volume $c_v(T,v_0)$ for all temperatures, but only one volume, e.g., in a constant volume calorimeter.[2] All other quantities follow from differential relations that are based on the Gibbs equation, and integration.

Above we have outlined the necessary measurements to fully determine all relevant thermodynamic properties. We close this section by pointing out that all properties can be determined if just one of the thermodynamic potentials is known, this is shown in the next example. Since all properties can be derived from the potential, the expression for the potential is sometimes called the *fundamental relation*.

16.6 Example: Gibbs Free Energy as Potential

In this example we consider a particular function for the Gibbs free energy $g(T,p)$, to show that knowledge of one potential allows to determine all relevant property relations, including all other potentials.

We consider the fundamental relation (A is a constant with the appropriate dimensions)

$$g(T,p) = -A\frac{T^4}{p} \,.$$

We first use that $g(T,p)$ is a potential (16.13), which gives the entropy and the specific volume as derivatives,

$$s(T,p) = -\left(\frac{\partial g}{\partial T}\right)_p = 4A\frac{T^3}{p} \,,$$

$$v(T,p) = \left(\frac{\partial g}{\partial p}\right)_T = A\frac{T^4}{p^2} \,.$$

The caloric equations of state then follow from the definition of $g = h - Ts = u + pv - Ts = f - pv$ as

[2] Or, alternatively, the measurement of the specific heat $c_p(T,p_0)$ at all temperatures but only one pressure p_0.

$$
\begin{aligned}
h(T,p) &= g + Ts = g - T\left(\frac{\partial g}{\partial T}\right)_p = 3A\frac{T^4}{p}\,,\\
u(T,p) &= h - pv = h - p\left(\frac{\partial g}{\partial p}\right)_T = 2A\frac{T^4}{p}\,,\\
f(T,p) &= g - pv = g - p\left(\frac{\partial g}{\partial p}\right)_T = -2A\frac{T^4}{p}\,.
\end{aligned}
$$

A switch of variables is obtained by solving the thermal equation of state for pressure,

$$
p(T,v) = \sqrt{A}\frac{T^2}{\sqrt{v}}\,,
$$

for which we find

$$
\begin{aligned}
s(T,v) &= 4\sqrt{A}T\sqrt{v}\,,\\
u(T,v) &= 2\sqrt{A}T^2\sqrt{v}\,,\\
h(T,v) &= 3\sqrt{A}T^2\sqrt{v}\,,\\
f(T,v) &= -2\sqrt{A}T^2\sqrt{v}\,,\\
g(T,v) &= -\sqrt{A}T^2\sqrt{v}\,.
\end{aligned}
$$

For the variables (T,v), the Helmholtz free energy $f(T,v)$ is a potential. It is easy to verify that the above expression for f fulfills

$$
s = -\left(\frac{\partial f}{\partial T}\right)_v \quad , \quad p = \left(\frac{\partial f}{\partial v}\right)_T \quad .
$$

Temperature $T(s,v)$ and the potentials $u(s,v)$ and $h(s,p)$ follow as

$$
T(s,v) = \frac{s}{4\sqrt{A}\sqrt{v}}\,,\quad u(s,v) = \frac{1}{8\sqrt{A}}\frac{s^2}{\sqrt{v}}\,,\quad h(s,p) = \frac{3}{4^{\frac{4}{3}}}\frac{1}{A^{\frac{1}{3}}}s^{\frac{4}{3}}p^{\frac{1}{3}}\,;
$$

the further evaluation of these potentials is left to the reader.

To determine the specific heat at constant volume we have to consider energy as function of temperature and volume, $u(T,v)$

$$
c_v(T,v) = \left(\frac{\partial u}{\partial T}\right)_v = \frac{\partial u(T,v)}{\partial T} = 4\sqrt{A}T\sqrt{v}\,.
$$

A shift in variables gives, e.g., $c_v(T,p) = 4A\frac{T^3}{p}$ or $c_v(s,p) = s$.

16.7 Compressibility, Thermal Expansion

The isothermal compressibility gives information about the volume change of a substance when pressure is changed isothermally, it is defined as

$$\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T \; ; \tag{16.37}$$

the minus sign is convention, and guarantees a positive value of the compressibility.

The coefficient of thermal expansion gives information about the volume change with temperature when the pressure is kept constant, it is defined as

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p \; . \tag{16.38}$$

We also define the coefficient

$$\beta = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_v \; , \tag{16.39}$$

which describes the increase of pressure with temperature in an isochoric process.

These and similar quantities are important for the design of thermal devices, e.g. for load calculations etc. Obviously, they can be determined from the measurement of the thermal equation of state $p(v, T)$. We shall show next that they are not independent.

For this, we begin with a mathematical exercise: Consider a function $z(x, y)$ and its differential

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \; . \tag{16.40}$$

We also have, by inversion, $x = x(y, z)$ and the corresponding differential

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \; . \tag{16.41}$$

Eliminating dx between the two equations gives

$$\left[1 - \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y\right] dz = \left[\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x\right] dy \; . \tag{16.42}$$

Since z and y can be varied independently, the factors in square brackets must vanish, and thus we have

$$\left(\frac{\partial z}{\partial x}\right)_y = \frac{1}{\left(\frac{\partial x}{\partial z}\right)_y} \quad , \quad \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1 \; . \tag{16.43}$$

These two equations hold for any choice of the functions[3] x, y, z; e.g., Eq. $(16.25)_2$ is a special case of $(16.43)_2$.

A special choice is $x = T$, $y = v$, $z = p$ so that

$$1 = -\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_p \left(\frac{\partial v}{\partial p}\right)_T = \frac{p\beta\kappa_T}{\alpha}\;; \tag{16.44}$$

this shows that the coefficients introduced above are dependent.

As an example we consider the ideal gas where $pv = RT$. We find

$$\kappa_T = \frac{1}{p} \quad , \quad \alpha = \frac{1}{T} \quad , \quad \beta = \frac{1}{T}\;. \tag{16.45}$$

From (16.26) we find

$$c_p - c_v = \alpha\beta vpT = \kappa_T \beta^2 vp^2 T\;. \tag{16.46}$$

Below we shall see that thermodynamic stability implies $\kappa_T \geq 0$, and thus the above implies $c_p \geq c_v$. For incompressible substances the isothermal compressibility vanishes, $\kappa_T = 0$, and thus the specific heats at constant pressure and volume agree, $c_p = c_v = c$.

A relation between the isentropic and the isothermal compressibilities can be found by the following chain of arguments, which uses (16.37, 16.27, 16.43),

$$\begin{aligned}
\kappa_s &= -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_s = -\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_s \left(\frac{\partial T}{\partial p}\right)_s \\
&= -\frac{1}{v}\left[-\left(\frac{\partial s}{\partial T}\right)_v \left(\frac{\partial v}{\partial s}\right)_T\right]\left(\frac{\partial T}{\partial p}\right)_s \\
&= \frac{c_v}{Tv}\left[\left(\frac{\partial v}{\partial p}\right)_T \left(\frac{\partial p}{\partial s}\right)_T\right]\left(\frac{\partial T}{\partial p}\right)_s \\
&= -\frac{c_v}{T}\kappa_T\left[-\left(\frac{\partial T}{\partial s}\right)_p\right] = \frac{c_v}{c_p}\kappa_T\;.
\end{aligned} \tag{16.47}$$

16.8 Example: Van der Waals Gas

The van der Waals equation (6.29) was developed to describe non-ideal gases, it reads

$$p = \frac{RT}{v - b} - \frac{a}{v^2}\;. \tag{16.48}$$

Here, the constant b accounts for the reduction of the volume accessible for a gas particle due to the finite size of the other molecules, and the constant

[3] In particular the first equation implies $\left(\frac{\partial z}{\partial y}\right)_x = 1/\left(\frac{\partial y}{\partial z}\right)_x$ and $\left(\frac{\partial x}{\partial y}\right)_z = 1/\left(\frac{\partial y}{\partial x}\right)_z$ as well, which were used to find the second equation.

a accounts for the reduction in pressure due to attractive forces between the particles. In ideal gases, the specific volume is relatively high, so that $b \ll v$ and $a \ll v^2$, in which case the equation reduces to the ideal gas law $p = \frac{RT}{v}$.

While the van der Waals equation offers intuitive insight into the deviation from ideal gas behavior, it only offers a qualitative description of real gas behavior, including, as will be seen later, phase changes. Thus, despite its quantitative inaccuracy, it serves as an important example to study thermodynamic principles and methods.

16.8.1 Determination of Constants *a*, *b*

The constants a and b are related to microscopic quantities, namely the eigenvolume of gas molecules, and the interaction potential between gas molecules. Their values a, b can be determined from property data at the critical point.

The critical isotherm has a horizontal inflection point at the critical point, so that

$$\left(\frac{\partial p}{\partial v}\right)_{T,cr} = \left(\frac{\partial^2 p}{\partial v^2}\right)_{T,cr} = 0\,. \tag{16.49}$$

Thus, together with the van der Waals equation (16.48) itself evaluated at the critical point, we have three conditions to be fulfilled at the critical point, which gives, after a brief calculation,

$$p_{cr} = \frac{1}{27}\frac{a}{b^2} \quad , \quad v_{cr} = 3b \quad , \quad RT_{cr} = \frac{8}{27}\frac{a}{b}\,. \tag{16.50}$$

At the critical point helium and water have the following properties:

$$\begin{array}{ll} \text{helium:} & T_{cr} = 5.3\,\mathrm{K} \;\;, \; p_{cr} = 0.23\,\mathrm{MPa} \;, \; v_{cr} = 1.445 \times 10^{-2}\,\frac{\mathrm{m}^3}{\mathrm{kg}} \;, \\ \text{water:} & T_{cr} = 647.3\,\mathrm{K} \;, \; p_{cr} = 22.09\,\mathrm{MPa} \;, \; v_{cr} = 3.156 \times 10^{-3}\,\frac{\mathrm{m}^3}{\mathrm{kg}} \;, \end{array} \tag{16.51}$$

from which one finds the constants as

$$\begin{array}{ll} \text{helium:} & a = 144.07\frac{\mathrm{m}^5}{\mathrm{s}^2\,\mathrm{kg}} \;, \; b = 4.817 \times 10^{-3}\,\frac{\mathrm{m}^3}{\mathrm{kg}} \;, \; R = 1672\frac{\mathrm{J}}{\mathrm{kg\,K}} \;, \\ \text{water:} & a = 660.1\frac{\mathrm{m}^5}{\mathrm{s}^2\,\mathrm{kg}} \;, \; b = 1.0526 \times 10^{-3}\,\frac{\mathrm{m}^3}{\mathrm{kg}} \;, \; R = 287\frac{\mathrm{J}}{\mathrm{kg\,K}} \;. \end{array} \tag{16.52}$$

The actual values for the gas constants of helium and water are $2079\frac{\mathrm{J}}{\mathrm{kg\,K}}$ and $462\frac{\mathrm{J}}{\mathrm{kg\,K}}$, respectively, and we see that the van der Waals equation predicts wrong values of the gas constants, with an error of about 20% for helium and 38% for water. The bigger error for water can be attributed to the more complex character of the dipole water molecules and their interaction among themselves, which makes them, other than the monatomic "spherical" helium atoms, not well suited for the arguments on interaction and eigenvolume that lead to the van der Waals equation.

The derivation of the van der Waals equation shows that the eigenvolume of a particle v_0 is related to the constant b as $v_0 = \frac{1}{2}bM/N_A$ where M is the molar mass and $N_A = 6.022 \times 10^{23}\frac{1}{\mathrm{mol}}$ is the Avogadro constant. Assuming spherical particles, the corresponding molecule diameter is

$$d_0 = \sqrt[3]{\frac{6}{\pi}v_0} = \sqrt[3]{\frac{3}{\pi}\frac{bM}{N_A}}\,, \tag{16.53}$$

which gives $d_0^{\mathrm{He}} = 3.126\times10^{-10}\,\mathrm{m}$ and $d_0^{\mathrm{H_2O}} = 3.11\times10^{-10}\,\mathrm{m}$. While certainly not exact, this numbers give a good indication of the molecule size.

16.8.2 Isotherms

When dimensionless pressure, volume and temperature are introduced by means of critical point data as

$$\pi = \frac{p}{p_{cr}} \quad , \quad \upsilon = \frac{v}{v_{cr}} \quad , \quad \tau = \frac{T}{T_{cr}}\,, \tag{16.54}$$

use of (16.50) gives the dimensionless van der Waals equation

$$\pi = \frac{8\tau}{3\upsilon - 1} - \frac{3}{\upsilon^2}\,. \tag{16.55}$$

In this dimensionless form, the equation is independent of the type of gas, all factors are independent of the type of gas. This somewhat surprising finding is known as the principle of corresponding states.

Figure 16.1 shows isothermal lines in the π-υ-diagram (i.e., the dimensionless p-v-diagram). The critical isotherm ($\tau = 1$) exhibits the horizontal inflection point at the critical point ($\pi = \upsilon = 1$). At supercritical temperatures ($\tau > 1$), the isotherms are monotonically decreasing with volume, and for large temperatures they agree with the curves from the ideal gas law.

For sub-critical temperatures, however, the curves are non-monotonic; in particular there is a portion of the curves where $\left(\frac{\partial v}{\partial p}\right)_T \geq 0$, which means that the isothermal compressibility is negative, $\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T < 0$. In the next chapter we will see that thermodynamic stability requires positive compressibility, $\kappa_T \geq 0$. Thus, these portions of the curves are unstable and cannot be attained. In Section 17.8 it will be seen how these unstable states are bridged by splitting of the van der Waals fluid into liquid and vapor phases.

For sufficiently small temperatures the isothermal curves predict negative pressure. States of negative pressure are unstable, but can be reached by very careful experiments in which they appear to be metastable.

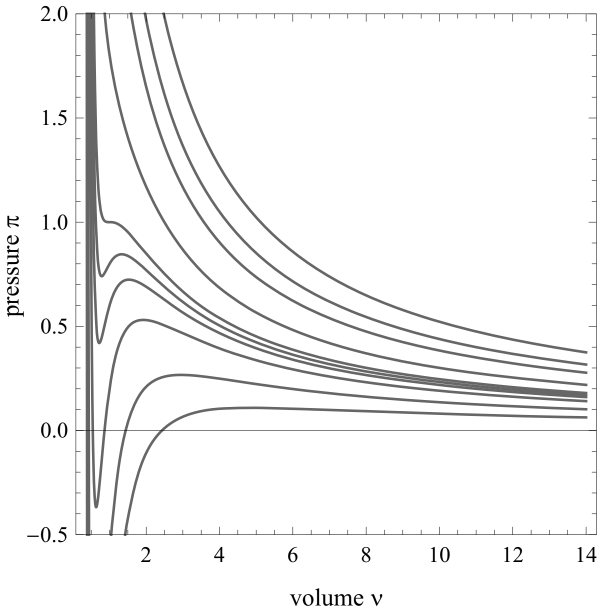

Fig. 16.1 Isotherms of the dimensionless van der Waals equation, for $\tau = 0.4, 0.6, 0.8, 0.9, 1.0, 1.2, 1.5, 1.7, 2.0$

16.8.3 Internal Energy and Entropy

Next we determine property relations for energy and entropy of the van der Waals gas. By inserting the van der Waals equation (16.48) into (16.17), we find

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p = \frac{a}{v^2}\,, \tag{16.56}$$

and from (16.31) we find

$$\left(\frac{\partial c_v}{\partial v}\right)_T = \frac{\partial}{\partial T}\left(\frac{\partial u}{\partial v}\right) = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0\,. \tag{16.57}$$

This implies that for a van der Waals gas, as for the ideal gas, the specific heat depends only on temperature, but not on volume. Energy itself, other than for the ideal gas, has a dependence on volume. Insertion of the above into (16.32) and explicit integration over volume then gives the internal energy of the van der Waals gas as

$$u\left(T,v\right) - u\left(T_0,v_0\right) = \int_{T_0}^{T} c_v\left(T'\right)dT' - a\left(\frac{1}{v} - \frac{1}{v_0}\right)\,. \tag{16.58}$$

We recall that the coefficient a describes the influence of long range interaction between the particles. The above shows the explicit contribution of these interactions on the energy of the gas. For large volume, the average particle distance is very large, and the average particle-particle interaction energy vanishes.

To compute the entropy $s(T, v)$ we use the Gibbs equation,

$$Tds = du + pdv = \left(\frac{\partial u}{\partial T}\right)_v dT + \left[\left(\frac{\partial u}{\partial v}\right)_T + p\right] dv = c_v dT + \frac{RT}{v-b} dv \ , \tag{16.59}$$

where for the last equation the equation of state and the above result for internal energy were used. Integration gives

$$s(T, v) - s(T_0, v_0) = \int_{T_0}^{T} \frac{c_v(T')}{T'} dT' + R \ln \frac{v-b}{v_0 - b} \ . \tag{16.60}$$

As we have seen earlier, entropy measures the number of possible microscopic realizations of the macroscopic state of a gas. In the van der Waals gas, the volume accessible to a particle is reduced by the presence of the other particles (measured by the coefficient b), and this reduces the number of possible configurations, and thus the entropic contribution from volume. For large volumes, $v - b \simeq v$, i.e., the contribution of particle volume can be ignored.

16.9 Joule-Thomson Coefficient

In a throttling process, the pressure drops while the enthalpy stays constant, the process is isenthalpic and irreversible. The temperature, however, may rise, fall, or stay constant. The Joule-Thomson coefficient $(\partial T/\partial p)_h$ describes the change of temperature with pressure in an isenthalpic process.

With the choice $x = h$, $y = p$, $z = T$, the relation $(16.43)_2$ gives an expression for the coefficient,

$$\left(\frac{\partial T}{\partial p}\right)_h = -\frac{1}{c_p}\left(\frac{\partial h}{\partial p}\right)_T \ . \tag{16.61}$$

Use of the relation (16.19) and the definition of the coefficient of thermal expansion α (16.38) gives

$$\left(\frac{\partial T}{\partial p}\right)_h = \frac{vT}{c_p}\left(\alpha - \frac{1}{T}\right) \ . \tag{16.62}$$

For an ideal gas where $\alpha = \frac{1}{T}$ we obtain $\left(\frac{\partial T}{\partial p}\right)_h = 0$; this reflects that enthalpy is a function only of temperature, which therefore must be constant in an isenthalpic process.

For a real gas, the curve where

$$\left(\frac{\partial T}{\partial p}\right)_h = 0 \quad \text{or} \quad \alpha = \frac{1}{T} \,, \tag{16.63}$$

is the inversion curve, it separates states where the temperature increases or decreases in throttling processes.

16.10 Example: Inversion Curve for the Van der Waals Gas

We compute the inversion curve for the van der Waals gas in the dimensionless variables π, υ, τ, where the condition assumes the form $\alpha = \frac{1}{\upsilon}\left(\frac{\partial \upsilon}{\partial \tau}\right)_\pi = \frac{1}{\tau}$, or

$$\upsilon \left(\frac{\partial \tau}{\partial \upsilon}\right)_\pi = \tau \,.$$

By solving the dimensionless van der Waals equation (16.55) for τ, inserting it into the above on both sides, and performing the derivatives, we find the relation between pressure and volume on the inversion curve,

$$\pi_{\text{inv}} = \frac{18}{\upsilon} - \frac{9}{\upsilon^2} \,.$$

Eliminating π with the van der Waals equation gives the inversion relation between τ and υ,

$$\tau_{\text{inv}} = \frac{3}{4}\left(3 - \frac{1}{\upsilon}\right)^2 \quad \text{or} \quad \upsilon_{\text{inv}} = \frac{1}{3 - 2\sqrt{\frac{\tau}{3}}} \,.$$

The above can be combined to

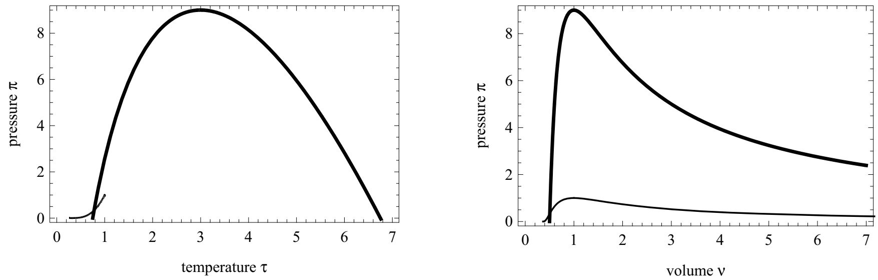

Fig. 16.2 Inversion curves for the van der Waals gas in π-τ- and π–υ-diagrams. The π-τ-diagram also shows the saturation line, and the π–υ-diagram shows the two phase region (thinner lines).

$$\pi_{\mathrm{inv}} = 24\sqrt{3\tau} - 12\tau - 27 \; .$$

The corresponding curves in the π-τ- and π-υ-diagrams are shown in Fig. 16.2, with respect to saturation lines, which will be determined in Sec. 17.9. For states below the curve the Joule-Thomson coefficient $\left(\frac{\partial T}{\partial p}\right)_h$ is positive, so that pressure reduction leads to cooling.

Problems

16.1. Fundamental Relation for Ideal Gas
Internal energy and entropy of an ideal gas with constant specific heats are $u = c_v T$, $s = c_v \ln \frac{T}{T_0} + R \ln \frac{v}{v_0}$. Determine the fundamental relations $u(s, v)$, $h(s, p)$, $f(T, v)$ and $g(T, p)$. Take the appropriate first derivatives of all to verify that they are potentials.

16.2. Fundamental Relation for Ideal Incompressible Liquid
Internal energy and entropy of an ideal incompressible liquid with constant specific heat are $u = cT$, $s = c \ln \frac{T}{T_0}$. Determine the fundamental relations $u(s, v)$, $h(s, p)$, $f(T, v)$ and $g(T, p)$. Take the appropriate first derivatives of all to verify that they are potentials.

16.3. Ideal Gas Table (Air)
The specific heat of air is in good accuracy given as

$$\bar{c}_p(T) = a + bT + cT^2 + dT^3 + \frac{e}{T^2} \; ,$$

with the constants:
for $T < 1000\,\mathrm{K}$:

$$a = 30.0051 \frac{\mathrm{kJ}}{\mathrm{kmol\,K}} \; , \quad b = -8.86766 \times 10^{-3} \frac{\mathrm{kJ}}{\mathrm{kmol\,K^2}} \; ,$$
$$c = 2.212730 \times 10^{-5} \frac{\mathrm{kJ}}{\mathrm{kmol\,K^3}} \; , \quad d = -1.02450 \times 10^{-8} \frac{\mathrm{kJ}}{\mathrm{kmol\,K^4}} \; ,$$
$$e = 8.38737 \times 10^{2} \frac{\mathrm{kJ\,K}}{\mathrm{kmol}} \; ;$$

for $1000\,\mathrm{K} < T < 2200\,\mathrm{K}$:

$$a = 36.7781 \frac{\mathrm{kJ}}{\mathrm{kmol\,K}} \; , \quad b = -3.90661 \times 10^{-3} \frac{\mathrm{kJ}}{\mathrm{kmol\,K^2}} \; ,$$
$$c = 3.46633 \times 10^{-6} \frac{\mathrm{kJ}}{\mathrm{kmol\,K^3}} \; , \quad d = -7.46611 \times 10^{-10} \frac{\mathrm{kJ}}{\mathrm{kmol\,K^4}} \; ,$$
$$e = -2.52571 \times 10^{6} \frac{\mathrm{kJ\,K}}{\mathrm{kmol}} \; .$$

1. Use the above data to prepare a table with the values of $\bar{u}(T)$, $\bar{h}(T)$, $\bar{s}^0(T)$ for air in the temperature range 230 – 2200 K. Adjust enthalpy and entropy so that $\bar{h}(300\,\mathrm{K}) = 8693.5\frac{\mathrm{kJ}}{\mathrm{kmol}}$ and $\bar{s}(T_0 = 298.15\,\mathrm{K}, p_0 = 1\,\mathrm{bar}) = 206.565\frac{\mathrm{kJ}}{\mathrm{kmol\,K}}$.
2. For easy handling of isentropic processes, it is convenient to have the relative pressure p_r and the relative volume v_r in the tables, see Sec. 7.5. Review their definition, and add them to your table as well.

16.4. Ideal Gas Table (H_2O)

When water vapor can be considered as ideal gas, its specific heat is in good accuracy given in polynomial form as

$$\bar{c}_p(T) = a + bT + cT^2 + dT^3 \,,$$

with the constants

$$a = 32.24\frac{\mathrm{kJ}}{\mathrm{kmol\,K}} \;,\quad b = 0.1923 \times 10^{-2}\frac{\mathrm{kJ}}{\mathrm{kmol\,K}^2} \,,$$
$$c = 1.055 \times 10^{-5}\frac{\mathrm{kJ}}{\mathrm{kmol\,K}^3} \;,\quad d = -3.595 \times 10^{-9}\frac{\mathrm{kJ}}{\mathrm{kmol\,K}^4} \,.$$

1. Use this data to prepare a table with the values of $\bar{u}(T)$, $\bar{h}(T)$, $\bar{s}^0(T)$ for water vapor in the temperature range 273 – 1800 K. Chose the energy and entropy constants such that you have agreement (as close as possible) with the table for water vapor as an ideal gas.
2. Next make tables for $u(T)$, $h(T)$, $s(T,p)$, for various values of p. Readjust the integration constants thus that your data matches the tables for superheated steam at $T = 50\,°\mathrm{C}$, $p = 0.01\,\mathrm{MPa}$. Make sets of tables at different pressures to compare with actual steam tables. Discuss the validity of the ideal gas assumption for vapor for high and low pressures, and high and low temperatures.

16.5. Thermodynamic Potential for a Gas

The Gibbs free energy of a gas is given as (a, b, c are constants with appropriate units)

$$g(T,p) = a\left(T - T\ln\frac{T}{T_0}\right) - \frac{b}{2}T^2 - \frac{c}{6}T^3 + RT\ln\frac{p}{p_0} \,.$$

1. Determine the equations of state for entropy $s(T,p)$, specific volume $v(T,p)$, enthalpy $h(T,p)$, internal energy $u(T,p)$, Helmholtz free energy $f(T,p)$.
2. Determine the equations of state for entropy $s(T,v)$, specific volume $v(T,v)$, enthalpy $h(T,v)$, internal energy $u(T,v)$, Helmholtz free energy $f(T,v)$.
3. Determine the specific heat at constant pressure, $c_p(T,p)$.
4. Determine the specific heat at constant volume, $c_v(T,v)$.

16.6. Thermodynamic Potential
The Helmholtz free energy of a substance is given as (A is a positive constant–determine its unit!)

$$f(T, v) = -AT^{\alpha}v^{\beta} \ .$$

1. Determine the equations of state for entropy $s(T, v)$, pressure $p(T, v)$, internal energy $u(T, v)$, enthalpy $h(T, v)$, Gibbs free energy $g(T, v)$.
2. Thermodynamic stability requires positive specific heat $c_v \geq 0$, and positive isothermal compressibility $\kappa_T \geq 0$. Use these requirements to identify the possible ranges of the exponents α and β.

16.7. Isothermal Compressibility and Thermal Expansion
Use tabulated data for superheated water vapor to estimate the isothermal compressibility κ_T and the coefficient of thermal expansion α at 600 °C and 7.0 MPa. Compare to the ideal gas values of $\kappa_{T,id.gas} = 1/p$ and $\alpha = 1/T$. Also determine the factor β from tabulated values, and test how well your approximations fulfill the relation $\frac{p\beta\kappa_T}{\alpha} = 1$.

16.8. Isothermal Compressibility
Use tabulated data for superheated vapor of R134a to estimate the isothermal compressibility κ_T at 60 °C and 1.4 MPa. Compare to the ideal gas value of $\kappa_{T,\mathrm{id.gas}} = 1/p$. Is it easier to compress ideal gas or R134a (at this state)? Why is that?

16.9. Coefficient of Thermal Expansion and Joule-Thomson Coefficient
Use tabulated data for superheated water vapor to estimate the specific heat at constant pressure, c_p, and the coefficient of thermal expansion, α, at 550 °C and 20 MPa. Use your results to determine the Joule-Thomson coefficient at the same state. When the vapor is throttled, will the temperature go up or down?

16.10. Measuring the Coefficient of Thermal Expansion
In the temperature range between 0 °C and 50 °C the coefficient of volume expansion of a liquid L is measured as $\alpha_L = 1.2 \times 10^{-3}\frac{1}{\mathrm{K}}$. To measure the coefficient of volume expansion for a solid S, the following experiment is conducted: A cylinder made of S is immersed in L and the percentage of immersed volume of solid is measured at 0 °C and 50 °C as 82.1% and 86.6%, respectively. Use Archimedes' principle to determine the coefficient α_S from this data.

16.11. Thermosyphon
In warm countries, one finds often a simple device for heating of water, the thermosyphon.

Solar radiation provides a heat flux $\dot{Q}$ which heats water. Since warm water has a smaller mass density than cold water, the heated water will rise. The goal is to compute the mass flow $\dot{m}$ and the temperature difference $T_t - T_b$ that will be observed.

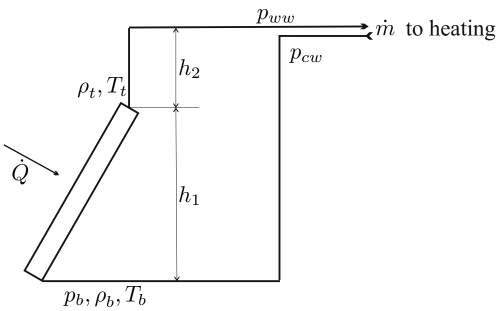

Fig. 16.3 Thermosyphon

1. Give arguments that $\frac{\rho_b-\rho_t}{\rho_b} = \alpha\,(T_t - T_b)$ where α is the thermal expansion coefficient of water.
2. Assume that the density is a linear function of height between 0 and h_1 and show that the difference between the pressures in warm and cold water is given by $\Delta p = p_{ww} - p_{cw} = (\rho_b - \rho_t)\, g\left(\frac{1}{2}h_1 + h_2\right)$. This refers to the pressure difference at rest, when $\dot{m} = 0$.
3. When the water is allowed to flow, the pressure difference determined above is consumed by friction. The law of Hagen-Poiseuille relates the volume flow and the pressure drop in a pipe of radius R and length L as $\dot{V} = \frac{\pi R^4}{8\eta L}\Delta p$, where η is the viscosity. The first law for the collector gives a relation between mass flow and temperature difference, $\dot{Q} = \dot{m}c_w\,(T_t - T_b)$. Combine all results to obtain equations for the temperature difference and the mass flow. Discuss what parameters must be increased to raise mass flow or temperature difference.
4. The maximum of solar radiation is $1300\frac{\mathrm{W}}{\mathrm{m}^2}$. Consider a collector with an area of $1\,\mathrm{m}^2$, and the data below to compute the temperature difference and mass flow.

$$R = 1\,\mathrm{cm}\ ,\ L = 10\,\mathrm{m}\ ,\ h_1 = 1/\sqrt{2}\,\mathrm{m}\ ,\ h_2 = 0.5\,\mathrm{m}\ ,$$
$$c_w = 4.18\frac{\mathrm{kJ}}{\mathrm{kg\,K}}\ ,\ \eta = 10^{-3}\frac{\mathrm{kg}}{\mathrm{m\,s}}\ ,\ \alpha = 2\times 10^{-4}\frac{1}{\mathrm{K}}\ .$$

16.12. Van der Waals Equation

Go through the arguments of Sec. 16.8 step by step to derive Eq. (16.50). Use critical point data for argon, oxygen, nitrogen to compute their van der Waals constants. Compare the values for R with their actual values, and discuss. Plot isotherms in a p-v-diagram. Also follow step by step through the arguments of Sec. 16.10 to determine and plot the inversion curve.