

14

Thermodynamic Identities

Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don't understand it, but by that time you are so used to it, it doesn't bother you any more.

Arnold Sommerfeld

14.1 Small Changes and Partial Derivatives

Many of the questions that arise in thermodynamics concern the effects of small perturbations on the values of the parameters describing the system. Even when the interesting questions concern large changes, the best approach to calculations is usually through adding up a series of small changes. For this reason, much of thermodynamics is concerned with the response of a system to small perturbations. Naturally, this takes the mathematical form of calculating partial derivatives.

Ultimately, the values of some partial derivatives must be found either from experiment or from the more fundamental theory of statistical mechanics. However, the power of thermodynamics is that it is able to relate different partial derivatives through general identities that are valid for all thermodynamic systems. Then, we might be able to relate a partial derivative that is difficult to calculate or measure to one that is easy to calculate or measure. In this chapter we will develop the mathematical tools needed to derive such thermodynamic identities.

14.2 A Warning about Partial Derivatives

For much of physics, partial derivatives are fairly straightforward: if we want to calculate the partial derivative with respect to some variable, we treat all other variables as constants and take the derivative in the usual way.

However, in thermodynamics it is rarely obvious what the ‘other’ variables are. Consequently, it is *extremely* important to specify explicitly which variables are being held constant when taking a partial derivative.

For example, consider the innocent-looking partial derivative, $\partial U / \partial V$, for a classical ideal gas. If we hold T constant,

$$\left(\frac{\partial U}{\partial V}\right)_{T,N} = \frac{\partial}{\partial V} \left(\frac{3}{2} N k_B T\right) = 0, \quad (14.1)$$

but if we hold P constant,

$$\left(\frac{\partial U}{\partial V}\right)_{P,N} = \frac{\partial}{\partial V} \left(\frac{3}{2} P V\right) = \frac{3}{2} P. \quad (14.2)$$

When S is held constant we can use the equation $dU = TdS - PdV$ to see that

$$\left(\frac{\partial U}{\partial V}\right)_{S,N} = -P. \quad (14.3)$$

We find three different answers—one positive, one negative, and one zero—just from changing what we are holding constant!

Don't forget to write explicitly what is being held constant in a partial derivative!

14.3 First and Second Derivatives

Since you memorized eq. (10.27) long ago, you know the first derivatives of the fundamental relation in the energy representation,

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T \quad (14.4)$$

$$\left(\frac{\partial U}{\partial V}\right)_{S,N} = -P \quad (14.5)$$

$$\left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu. \quad (14.6)$$

Since you also know how to find the Legendre transform of the differential form of a fundamental relation, you know the first derivatives of the Gibbs free energy:

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S \quad (14.7)$$

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V \quad (14.8)$$

$$\left(\frac{\partial G}{\partial N}\right)_{T,P} = \mu. \quad (14.9)$$

Essentially, we find various subsets of U, S, T, V, P, μ , and N when we take a first partial derivative of the fundamental relation. Second derivatives provide information about how these quantities change when other quantities are varied.

There are clearly many different second derivatives that can be constructed from all the variables we have introduced—especially when we remember that holding different quantities constant produces different partial derivatives. However, the number of *independent* second derivatives is limited. This is the fundamental reason for the existence of thermodynamic identities.

If we consider the fundamental relation in the energy representation for a simple system with a single component, first derivatives can be taken with respect to the three independent variables: S , V , and N . That means that there are a total of six independent second derivatives that can be formed. All other second derivatives must be functions of these six.

In many applications the composition of the system is fixed, so that there are only two independent variables. This means that even if we are dealing with a multi-component system, there are only three independent second derivatives. For example, if we consider $U(S, V, N)$ with N held constant, the independent second derivatives are:

$$\left(\frac{\partial^2 U}{\partial S^2}\right), \quad (14.10)$$

$$\left(\frac{\partial^2 U}{\partial S \partial V}\right) = \left(\frac{\partial^2 U}{\partial V \partial S}\right), \quad (14.11)$$

and

$$\left(\frac{\partial^2 U}{\partial V^2}\right). \quad (14.12)$$

This is a key observation, because it implies that only three measurements are needed to predict the results of *any* experiment involving small changes. This can be crucial if the quantity you want to determine is very difficult to measure directly. By relating it to things that are easy to measure, you can both increase accuracy and save yourself a lot of work.

On the other hand, knowing that everything is related is not the same as knowing what that relationship is. The subject of thermodynamic identities is the study of how to reduce any partial derivative to a function of a convenient set of standard partial derivatives.

14.4 Standard Set of Second Derivatives

The three standard second derivatives are:

The coefficient of thermal expansion

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P,N}. \quad (14.13)$$

The isothermal compressibility

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T,N}. \quad (14.14)$$

The minus sign in the definition is there to make κ_T positive, since the volume decreases when pressure increases.

The specific heat per particle at constant pressure

$$c_P = \frac{T}{N} \left(\frac{\partial S}{\partial T} \right)_{P,N}. \quad (14.15)$$

The specific heat per particle at constant volume

$$c_V = \frac{T}{N} \left(\frac{\partial S}{\partial T} \right)_{V,N}. \quad (14.16)$$

Well, yes, I have listed four of them.

However, because there are only three independent second derivatives, we will be able to find a universal equation linking them. Usually, the first three are the easiest to measure, and they are taken as fundamental. Trying to measure c_V for iron is difficult, but c_P is easy. However, measuring c_V for a gas might be easier than measuring c_P , so it has been included.

If we are interested in the properties of a particular system we might also use the ‘heat capacity’, denoted by a capital C ; that is, $C_P = N c_P$ and $C_V = N c_V$.

It should be noted that I have defined c_P and c_V as specific heats per particle. It is also quite common to speak of the specific heat per mole, for which division by the number of moles would appear in the definition instead of division by N . It is also sometimes useful to define a specific heat per unit mass.

Our goal for the rest of the chapter is to develop methods for reducing all possible thermodynamic second derivatives to combinations of the standard set.

The four second derivatives listed in eqs. (14.13) through (14.16) should be memorized. While they are not as important as eq. (10.27), it is useful not to have to consult them when deriving thermodynamic identities. The brief time spent memorizing them will be repaid handsomely.

14.5 Maxwell Relations

The first technique we need is a direct application of what you learned about exact differentials in Section 10.3.1. Since every differential representation of the fundamental relation is an exact differential, we can apply eq. (10.11) to all of them.

For example, start with the differential form of the fundamental relation in the energy representation, eq. (10.27), which you have long since memorized,

$$dU = TdS - PdV + \mu dN. \quad (14.17)$$

If N is held constant, this becomes

$$dU = TdS - PdV. \quad (14.18)$$

Applying the condition for dU being an exact differential produces a new identity,

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}. \quad (14.19)$$

Eq. (14.19) and all other identities derived in the same way are called Maxwell relations. They all depend on the condition in eq. (10.11) that the differential of a thermodynamic potential be an exact differential.

The thing that makes Maxwell relations so easy to use is that the differential forms of the fundamental relation in different representations are all simply related. For example, to find dF from dU , simply switch T and S in eq. (14.17) and change the sign of that term,

$$dF = -SdT - PdV + \mu dN. \quad (14.20)$$

From this equation, we find another Maxwell relation,

$$-\left(\frac{\partial S}{\partial V}\right)_{T,N} = -\left(\frac{\partial P}{\partial T}\right)_{V,N}. \quad (14.21)$$

It is even easy to find exactly the right Maxwell relation, given a particular partial derivative that you want to transform, by finding the right differential form of the fundamental relation.

For example, suppose you want a Maxwell relation to transform the following partial derivative:

$$\left(\frac{\partial T}{\partial P}\right)_{S,\mu} = \left(\frac{\partial ?}{\partial ?}\right)_{?,?}. \quad (14.22)$$

Begin with eq. (14.17) and choose the Legendre transform that

- leaves T in front of dS , so that T is being differentiated;
- changes $-PdV$ to VdP , so that the derivative is with respect to P ; and
- changes μdN to $-Nd\mu$, so that μ is held constant.

The result is the differential form of the fundamental equation in the $U[P,\mu]$ representation

$$dU[P,\mu] = TdS + VdP - Nd\mu. \quad (14.23)$$

Now apply eq. (10.11) with $d\mu = 0$,

$$\left(\frac{\partial T}{\partial P}\right)_{S,\mu} = \left(\frac{\partial V}{\partial S}\right)_{P,\mu}. \quad (14.24)$$

Note that you do not even have to remember which representation you are transforming into to find Maxwell relations. The thermodynamic potential $U[P,\mu]$ is not used sufficiently to have been given a separate name, but you do not need to know its name to derive the Maxwell relation in eq. (14.24).

You do have to remember that the Legendre transform changes the sign of the differential term containing the transformed variables. But that is easy.

14.6 Manipulating Partial Derivatives

Unfortunately, Maxwell relations are not sufficient to derive all thermodynamic identities. We will still need to manipulate partial derivatives to put them into more convenient forms. A very elegant way of doing this is provided by the use of Jacobians.

We do have to introduce some new mathematics at this point, but the result will be that thermodynamic identities become quite easy to derive—perhaps even fun.

14.6.1 Definition of Jacobians

Jacobians are defined as the determinant of a matrix of derivatives:

$$\frac{\partial(u,v)}{\partial(x,y)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix} = \frac{\partial u}{\partial x} \frac{\partial v}{\partial y} - \frac{\partial u}{\partial y} \frac{\partial v}{\partial x}. \quad (14.25)$$

Since we have only the two variables, x and y , in this definition, I have suppressed the explicit indication of which variables are being held constant. This is an exception that should not be imitated.

The definition in eq. (14.25) can be extended to any number of variables, but there must be the same number of variables in the numerator and denominator; the determinant must involve a square matrix.

14.6.2 Symmetry of Jacobians

The Jacobian changes sign when any two variables in the numerator or the denominator are exchanged, because the sign of a determinant changes when two rows or two columns are switched. (Variables *cannot* be exchanged between numerator and denominator.)

$$\frac{\partial(u,v)}{\partial(x,y)} = -\frac{\partial(v,u)}{\partial(x,y)} = \frac{\partial(v,u)}{\partial(y,x)} = -\frac{\partial(u,v)}{\partial(y,x)}. \quad (14.26)$$

This also works for larger Jacobians, although we will rarely need them,

$$\frac{\partial(u,v,w,s)}{\partial(x,y,z,t)} = -\frac{\partial(v,u,w,s)}{\partial(x,y,z,t)} = \frac{\partial(v,u,w,s)}{\partial(y,x,z,t)}. \quad (14.27)$$

14.6.3 Partial Derivatives and Jacobians

Consider the Jacobian

$$\frac{\partial(u,y)}{\partial(x,y)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial y}{\partial x} & \frac{\partial y}{\partial y} \end{vmatrix}. \quad (14.28)$$

Since

$$\frac{\partial y}{\partial x} = 0 \quad (14.29)$$

and

$$\frac{\partial y}{\partial y} = 1 \quad (14.30)$$

we have

$$\frac{\partial(u,y)}{\partial(x,y)} = \left(\frac{\partial u}{\partial x} \right)_y. \quad (14.31)$$

This is the link between partial derivatives in thermodynamics and Jacobians.

We will also see it in an extended form with more variables held constant,

$$\frac{\partial(u,y,z)}{\partial(x,y,z)} = \left(\frac{\partial u}{\partial x}\right)_{y,z}. \quad (14.32)$$

For example:

$$\frac{\partial(V,T,N)}{\partial(P,T,N)} = \left(\frac{\partial V}{\partial P}\right)_{T,N}. \quad (14.33)$$

14.6.4 A Chain Rule for Jacobians

The usual chain rule for derivatives takes on a remarkably simple form for Jacobians:

$$\frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(u,v)}{\partial(r,s)} \frac{\partial(r,s)}{\partial(x,y)}. \quad (14.34)$$

To prove this, it is convenient to introduce a more compact notation,

$$\frac{\partial u}{\partial x} \equiv u_x. \quad (14.35)$$

Now we can write

$$\begin{aligned} \frac{\partial(u,v)}{\partial(r,s)} \frac{\partial(r,s)}{\partial(x,y)} &= \begin{vmatrix} u_r & u_s \\ v_r & v_s \end{vmatrix} \begin{vmatrix} r_x & r_y \\ s_x & s_y \end{vmatrix} \\ &= \begin{vmatrix} u_r r_x + u_s s_x & u_r r_y + u_s s_y \\ v_r r_x + v_s s_x & v_r r_y + v_s s_y \end{vmatrix} \\ &= \begin{vmatrix} u_x & u_y \\ v_x & v_y \end{vmatrix} \\ &= \frac{\partial(u,v)}{\partial(x,y)} \end{aligned} \quad (14.36)$$

which proves eq. (14.34).

14.6.5 Products of Jacobians

The following identities are very useful:

$$\frac{\partial(u,v)}{\partial(x,y)} \frac{\partial(a,b)}{\partial(c,d)} = \frac{\partial(u,v)}{\partial(c,d)} \frac{\partial(a,b)}{\partial(x,y)} = \frac{\partial(a,b)}{\partial(x,y)} \frac{\partial(u,v)}{\partial(c,d)}. \quad (14.37)$$

To prove them, we use eq. (14.34) which we showed to be an identity in the previous subsection,

$$\begin{aligned}\frac{\partial(u,v)}{\partial(x,y)} \frac{\partial(a,b)}{\partial(c,d)} &= \frac{\partial(u,v)}{\partial(r,s)} \frac{\partial(r,s)}{\partial(x,y)} \frac{\partial(a,b)}{\partial(r,s)} \frac{\partial(r,s)}{\partial(c,d)} \\ &= \frac{\partial(u,v)}{\partial(r,s)} \frac{\partial(r,s)}{\partial(c,d)} \frac{\partial(a,b)}{\partial(r,s)} \frac{\partial(r,s)}{\partial(x,y)} \\ &= \frac{\partial(u,v)}{\partial(c,d)} \frac{\partial(a,b)}{\partial(x,y)}.\end{aligned}\quad (14.38)$$

For many purposes, eq. (14.37) allows expressions of the form $\partial(x,y)$ to be manipulated almost as if they were algebraic factors.

14.6.6 Reciprocals of Jacobians

Reciprocals of Jacobians are both simple and useful.

Write the identity in eq. (14.34) with (x,y) set equal to (u,v) ,

$$\frac{\partial(u,v)}{\partial(u,v)} = \frac{\partial(u,v)}{\partial(r,s)} \frac{\partial(r,s)}{\partial(u,v)}\quad (14.39)$$

But

$$\frac{\partial(u,v)}{\partial(u,v)} = \begin{vmatrix} u_u & u_v \\ v_u & v_v \end{vmatrix} = \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix} = 1,\quad (14.40)$$

so that

$$\frac{\partial(u,v)}{\partial(r,s)} = 1 \left/ \frac{\partial(r,s)}{\partial(u,v)} \right.. \quad (14.41)$$

Using eq. (14.41) for reciprocals, we can express the chain rule from the previous section in a particularly useful alternative form

$$\frac{\partial(u,y)}{\partial(x,y)} = \frac{\partial(u,y)}{\partial(r,s)} \left/ \frac{\partial(x,y)}{\partial(r,s)} \right.. \quad (14.42)$$

Note that eq. (14.41), combined with eq. (14.31), gives us a useful identity for partial derivatives

$$\left(\frac{\partial u}{\partial x} \right)_y = 1 \left/ \left(\frac{\partial x}{\partial u} \right)_y \right.. \quad (14.43)$$

An important application of eq. (14.43) can occur when you are looking for a Maxwell relation for a derivative like the following:

$$\left(\frac{\partial V}{\partial S}\right)_{T,N}. \quad (14.44)$$

If you try to find a transform of the fundamental relation, $dU = TdS - Pdv + \mu dN$, you run into trouble because S is in the denominator of eq. (14.44) and T is being held constant. However, we use eq. (14.41) to take the reciprocal of eq. (14.44), for which a Maxwell relation can be found,

$${}^1 \left/ \left(\frac{\partial V}{\partial S}\right)_{T,N} \right. = \left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N}. \quad (14.45)$$

14.7 Working with Jacobians

As a first example of how to use Jacobians to derive thermodynamic identities, consider the partial derivative of pressure with respect to temperature, holding V and N constant,

$$\left(\frac{\partial P}{\partial T}\right)_{V,N}. \quad (14.46)$$

To simplify the notation, we will suppress the explicit subscript N .

The first step is always to take the partial derivative you wish to simplify, and express it as a Jacobian using eq. (14.31),

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\partial(P, V)}{\partial(T, V)}. \quad (14.47)$$

The next step is usually to insert $\partial(P, T)$ into the Jacobian, using either eq. (14.34) or eq. (14.42). The reason is that the second derivatives given in Section 14.4—which constitute the standard set—are all derivatives with respect to P , holding T constant, or with respect to T , holding P constant. Inserting $\partial(P, T)$ is a step in the right direction in either case,

$$\frac{\partial(P, V)}{\partial(T, V)} = \frac{\partial(P, V)}{\partial(P, T)} \left/ \frac{\partial(T, V)}{\partial(P, T)} \right.. \quad (14.48)$$

Next, we have to line up the variables in the Jacobians to produce the correct signs, remembering to change the sign of the Jacobian every time we exchange variables,

$$\frac{\partial(P, V)}{\partial(T, V)} = -\frac{\partial(P, V)}{\partial(P, T)} \left/ \frac{\partial(V, T)}{\partial(P, T)} \right. = -\frac{\partial(V, P)}{\partial(T, P)} \left/ \frac{\partial(V, T)}{\partial(P, T)} \right.. \quad (14.49)$$

The minus sign came from switching T and V in the second factor. I also switched both top and bottom in the first factor to bring it into the same order as the form given above. This is not really necessary, but it might be helpful as a memory aid.

Next, we can transform back to partial derivatives,

$$\left(\frac{\partial P}{\partial T}\right)_V = - \left(\frac{\partial V}{\partial T}\right)_P \Big/ \left(\frac{\partial V}{\partial P}\right)_T. \quad (14.50)$$

Using the standard expressions for the coefficient of thermal expansion

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_{P,N} \quad (14.51)$$

and the isothermal compressibility

$$\kappa_T = - \frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_{T,N} \quad (14.52)$$

eq. (14.50) becomes

$$\left(\frac{\partial P}{\partial T}\right)_V = -V\alpha / (-V\kappa_T) = \frac{\alpha}{\kappa_T}. \quad (14.53)$$

To see why eq. (14.53) might be useful, consider the properties of lead, which has a fairly small coefficient of expansion

$$\alpha(Pb) = 8.4 \times 10^{-5} K^{-1}. \quad (14.54)$$

Lead also has a small isothermal compressibility

$$\kappa_T(Pb) = 2.44 \times 10^{-6} Atm^{-1}. \quad (14.55)$$

Inserting these values into eq. (14.53), we find the change in pressure with temperature for a constant volume for lead

$$\left(\frac{\partial P}{\partial T}\right)_{V,N} = 34.3 Atm/K. \quad (14.56)$$

As might be expected, it is not easy to maintain lead at a constant volume as the temperature increases. A direct experiment to measure the change in pressure at constant volume would be extremely difficult. However, since α and κ_T are known, we can obtain the result in eq. (14.56) quite easily.

This is a relatively simple case. The most common additional complexity is that you might have to use a Maxwell relation after you have transformed the derivatives, but it must be confessed that some identities can be quite challenging to derive.

14.8 Examples of Identity Derivations

The following two examples illustrate further techniques for proving thermodynamic identities using Jacobians. They are of interest both for the methods used and for the identities themselves.

14.8.1 The Joule–Thomson Effect

In a ‘throttling’ procedure, gas is continuously forced through a porous plug with a high-pressure P_A on one side and a low-pressure P_B on the other. The initial and final states are in equilibrium. If we consider a volume V_A of gas on the left, it will take up a volume V_B after it passes to the right. The energy of this amount of gas on the right is determined by conservation of energy:

$$U_B = U_A + P_A V_A - P_B V_B. \quad (14.57)$$

Rearranging this equation, we find that the enthalpy is unchanged by the process, even though the process is clearly irreversible,

$$H_A = U_A + P_A V_A = U_B + P_B V_B = H_B. \quad (14.58)$$

If the pressure change is small, the temperature change is given by a partial derivative

$$dT = \left(\frac{\partial T}{\partial P} \right)_{H,N} dP. \quad (14.59)$$

The partial derivative in eq. (14.59) is called the Joule–Thomson coefficient, μ_{JT} .¹

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_{H,N}. \quad (14.60)$$

We can express the Joule–Thomson coefficient in terms of the standard set of derivatives using Jacobians

¹ James Prescott Joule (1818–1889) was a British physicist who had worked on the free expansion of gases, and William Thomson (1824–1907) was an Irish physicist who continued along the lines of Joule’s investigations and discovered the Joule–Thomson effect in 1852. Thomson was later elevated to the peerage with the title Baron Kelvin, and the Joule–Thomson effect is therefore sometimes called the Joule–Kelvin effect.

$$\begin{aligned}
 \left(\frac{\partial T}{\partial P}\right)_{H,N} &= \frac{\partial(T,H)}{\partial(P,H)} \\
 &= \frac{\partial(T,H)}{\partial(P,T)} \Bigg/ \frac{\partial(P,H)}{\partial(P,T)} \\
 &= -\left(\frac{\partial H}{\partial P}\right)_{T,N} \Bigg/ \left(\frac{\partial H}{\partial T}\right)_{P,N}.
 \end{aligned} \tag{14.61}$$

The derivative with respect to P can be evaluated by using the differential form of the fundamental relation in the enthalpy representation, (The term μdN is omitted because the total number of particles is fixed.)

$$dH = TdS + VdP \tag{14.62}$$

$$\begin{aligned}
 \left(\frac{\partial H}{\partial P}\right)_{T,N} &= T\left(\frac{\partial S}{\partial P}\right)_{T,N} + V\left(\frac{\partial P}{\partial P}\right)_{T,N} \\
 &= -T\left(\frac{\partial V}{\partial T}\right)_{P,N} + V \\
 &= -TV\alpha + V \\
 &= -V(T\alpha - 1).
 \end{aligned} \tag{14.63}$$

The proof of the Maxwell relation used in this derivation will be left as an exercise.

We can also transform the other partial derivative in eq. (14.61) using eq. (14.62),

$$\begin{aligned}
 \left(\frac{\partial H}{\partial T}\right)_{P,N} &= T\left(\frac{\partial S}{\partial T}\right)_{P,N} + V\left(\frac{\partial P}{\partial T}\right)_{P,N} \\
 &= Nc_P.
 \end{aligned} \tag{14.64}$$

Putting eqs. (14.61), (14.63), and (14.64) together, we find our final expression for the Joule–Thomson coefficient

$$\mu_{JT} = \frac{V}{Nc_P}(T\alpha - 1). \tag{14.65}$$

The Joule–Thomson effect is central to most refrigeration and air-conditioning systems. When the Joule–Thomson coefficient is positive, the drop in pressure across the porous plug produces a corresponding drop in temperature, for which we are often grateful in the summer.

14.8.2 c_P and c_V

The thermodynamic identity linking c_P and c_V has already been alluded to in Section 14.4. It is central to the reduction to the *three* standard partial derivatives by

eliminating c_V . This derivation is one of the relatively few times that an expansion of the Jacobian turns out to be useful in proving thermodynamic identities.

Begin the derivation with c_V , suppressing the subscript N for simplicity,

$$\begin{aligned} c_V &= \frac{T}{N} \left(\frac{\partial S}{\partial T} \right)_V \\ &= \frac{T}{N} \frac{\partial(S, V)}{\partial(T, V)} \\ &= \frac{T}{N} \frac{\partial(S, V)}{\partial(T, P)} \Big/ \frac{\partial(T, V)}{\partial(T, P)}. \end{aligned} \quad (14.66)$$

The denominator of the last expression can be recognized as the compressibility,

$$\frac{\partial(T, V)}{\partial(T, P)} = \frac{\partial(V, T)}{\partial(P, T)} = \left(\frac{\partial V}{\partial P} \right)_T = -V\kappa_T. \quad (14.67)$$

The Jacobian in the numerator of the last expression in eq. (14.66) can be expressed by expanding the defining determinant

$$\frac{\partial(S, V)}{\partial(T, P)} = \left(\frac{\partial S}{\partial T} \right)_P \left(\frac{\partial V}{\partial P} \right)_T - \left(\frac{\partial S}{\partial P} \right)_T \left(\frac{\partial V}{\partial T} \right)_P. \quad (14.68)$$

Now we can identify each of the four partial derivatives on the right of eq. (14.68):

$$\left(\frac{\partial S}{\partial T} \right)_P = \frac{Nc_P}{T} \quad (14.69)$$

$$\left(\frac{\partial V}{\partial P} \right)_T = -V\kappa_T \quad (14.70)$$

$$\left(\frac{\partial S}{\partial P} \right)_T = -\left(\frac{\partial V}{\partial T} \right)_P = -\alpha V \quad (14.71)$$

$$\left(\frac{\partial V}{\partial T} \right)_P = \alpha V. \quad (14.72)$$

In eq. (14.71), a Maxwell relation has been used to relate the partial derivative to α .

Putting the last six equations together, we obtain

$$c_P = c_V + \frac{\alpha^2 TV}{N\kappa_T} \quad (14.73)$$

which is the required identity.

Although it should not be necessary to memorize eq. (14.73), you should be able to derive it.

14.9 General Strategy

This section summarizes a useful strategy to reduce a given partial derivative to an algebraic expression containing only the three partial derivatives given in Section 14.4. These steps might be needed for attacking the most difficult derivations, but not all steps are necessary in most cases.

1. Express the partial derivative as a Jacobian.
2. If there are any thermodynamic potentials in the partial derivative, bring them to the numerator by applying eq. (14.42). Unless you have a good reason to do something else, insert $\partial(T, P)$ in this step.
3. Eliminate thermodynamic potentials if you know the derivative. For example:

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S.$$

4. Eliminate thermodynamic potentials by using the differential form of the fundamental relation. For example: if you want to evaluate

$$\left(\frac{\partial F}{\partial P}\right)_{T,N}$$

use

$$dF = -SdT - PdV + \mu dN$$

to find

$$\left(\frac{\partial F}{\partial P}\right)_{T,N} = -S\left(\frac{\partial T}{\partial P}\right)_{T,N} - P\left(\frac{\partial V}{\partial P}\right)_{T,N} + \mu\left(\frac{\partial N}{\partial P}\right)_{T,N}.$$

Note that the first and last terms on the right in this example vanish.

5. If the system is extensive, bring μ to the numerator and eliminate it using the Gibbs–Duhem relation, eq. (13.11)

$$d\mu = -\left(\frac{S}{N}\right)dT + \left(\frac{V}{N}\right)dP.$$

For example:

$$\left(\frac{\partial \mu}{\partial V}\right)_{S,N} = -\left(\frac{S}{N}\right)\left(\frac{\partial T}{\partial V}\right)_{S,N} + \left(\frac{V}{N}\right)\left(\frac{\partial P}{\partial V}\right)_{S,N}.$$

6. Move the entropy to the numerator using Jacobians and eliminate it by either identifying the partial derivative of the entropy as a specific heat if the derivative is with respect to T , or using a Maxwell relation if the derivative is with respect to pressure.
7. Bring V into the numerator and eliminate the partial derivative in favor of α or κ_T .
8. Eliminate c_V in favor of c_P , using the identity in eq. (14.73), derived in the previous section. (This last step is not always needed, since c_V is sometimes easier to measure than c_P .)

14.10 Problems

PROBLEM 14.1

Maxwell relations

Note: This assignment is useless if you just look up the answers in a textbook. You will not have a book during examinations, so you should do this assignment with book and notes closed.

Transform the following partial derivatives using Maxwell relations:

1.
$$\left(\frac{\partial \mu}{\partial V}\right)_{S,N} = \left(\frac{\partial ?}{\partial ?}\right)_{?,?}$$
2.
$$\left(\frac{\partial \mu}{\partial V}\right)_{T,N} = \left(\frac{\partial ?}{\partial ?}\right)_{?,?}$$
3.
$$\left(\frac{\partial S}{\partial P}\right)_{T,N} = \left(\frac{\partial ?}{\partial ?}\right)_{?,?}$$
4.
$$\left(\frac{\partial V}{\partial S}\right)_{P,N} = \left(\frac{\partial ?}{\partial ?}\right)_{?,?}$$
5.
$$\left(\frac{\partial N}{\partial P}\right)_{S,\mu} = \left(\frac{\partial ?}{\partial ?}\right)_{?,?}$$
6.
$$\left(\frac{\partial P}{\partial T}\right)_{S,N} = \left(\frac{\partial ?}{\partial ?}\right)_{?,?}$$
7.
$$\left(\frac{\partial N}{\partial P}\right)_{S,V} = \left(\frac{\partial ?}{\partial ?}\right)_{?,?}.$$

PROBLEM 14.2

A thermodynamic identity

Express the following thermodynamic derivative in terms of α, κ_T, c_V , and c_P using Jacobians.

$$\left(\frac{\partial T}{\partial P}\right)_{S,N} = ?.$$

PROBLEM 14.3

Prove the following thermodynamic identity

$$\left(\frac{\partial c_V}{\partial V}\right)_{T,N} = \frac{T}{N} \left(\frac{\partial^2 P}{\partial T^2}\right)_{V,N}.$$

PROBLEM 14.4

Express the following partial derivative in terms of the usual standard quantities

$$\left(\frac{\partial F}{\partial S}\right)_{T,N}.$$

PROBLEM 14.5

Yet another thermodynamic identity

Prove the following thermodynamic derivative and determine what should replace the question marks. Note that you do not have to reduce this to the standard expressions, but can leave it in terms of partial derivatives

$$c_V = -\frac{T}{N} \left(\frac{\partial P}{\partial T}\right)_{V,N} \left(\frac{\partial ?}{\partial ?}\right)_{S,N}.$$

PROBLEM 14.6

Compressibility identity

In analogy to the isothermal compressibility,

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_{T,N}$$

we can define the adiabatic compressibility,

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_{S,N}.$$

The name is due to the fact that $TdS = dQ$ for quasi-static processes.

In analogy to the derivation for the difference in the specific heats at constant pressure and constant temperature, derive the following thermodynamic identity:

$$\kappa_S = \kappa_T - \frac{TV\alpha^2}{Ncp}.$$

PROBLEM 14.7**Callen's horrible example of a partial derivative**

In his classic book on thermodynamics, Herbert Callen used the following derivative as an example:

$$\left(\frac{\partial P}{\partial U}\right)_{G,N}.$$

However, he did not complete the derivation. Your task is to reduce this partial derivative to contain only the standard partial derivatives α, κ_T, c_P , and c_V , and, of course, any of the first derivatives, T, S, P, V, μ , or N .

This derivation will require all the techniques that you have learned for transforming partial derivatives. Have fun!

PROBLEM 14.8**A useful identity**

Prove the identity:

$$\frac{\partial(V, S)}{\partial(T, P)} = \frac{NVc_V\kappa_T}{T}.$$

PROBLEM 14.9**The TdS equations**

Prove the following three TdS equations. [N is held constant throughout.]

1. First TdS equation

$$TdS = Nc_VdT + (T\alpha/\kappa_T)dV.$$

2. Second TdS equation

Prove:

$$TdS = Nc_PdT - TV\alpha dP.$$

3. Third TdS equation

Three forms:

$$TdS = Nc_P \left(\frac{\partial T}{\partial V}\right)_P dV + Nc_V \left(\frac{\partial T}{\partial P}\right)_V dP$$

or

$$TdS = \frac{Nc_P}{V\alpha} dV + Nc_V \left(\frac{\partial T}{\partial P}\right)_V dP$$

or

$$TdS = \frac{Nc_P}{V\alpha} dV + \frac{Nc_V\kappa_T}{\alpha} dP.$$

PROBLEM 14.10

Another useful identity

Since we will be using it in statistical mechanics, prove the following identity:

$$\left(\frac{\partial(\beta F)}{\partial \beta} \right)_{V,N} = U$$

where $\beta = \frac{1}{k_B T}$.
