Chapter II

USE OF JACOBIANS IN THERMODYNAMICS

Many students find that thermodynamics, although mathematically almost trivial, is nevertheless one of the most difficult subjects in their program. A large part of the blame for this lies in the extremely cumbersome partial derivative notation. In this chapter we develop a different mathematical scheme, with which thermodynamic derivations can be carried out more easily, and which gives a better physical insight into the meaning of thermodynamic relations.

2.1 Statement of the Problem

In fields other than thermodynamics, one usually starts out by stating explicitly what variables shall be considered the independent ones, and then uses partial derivatives without subscripts, the understanding being that all independent variables other than the ones explicitly present are held constant in the differentiation. This convention is used in most of mathematics and physics without serious misunderstandings. But in thermodynamics, one never seems to be able to maintain a fixed set of independent variables throughout a derivation, and it becomes necessary to add one or more subscripts to every derivative to indicate what is being held constant. The often-needed transformation from one constant quantity to another involves the relation

$$\left(\frac{\partial A}{\partial B}\right)_C = \left(\frac{\partial A}{\partial B}\right)_D + \left(\frac{\partial A}{\partial D}\right)_B \left(\frac{\partial D}{\partial B}\right)_C \qquad (2\text{-}1)$$

which, although it expresses a fact that is mathematically trivial, assumes such a complicated form in the usual notation that few people can remember it long enough to write it down after the book is closed.

As a further comment on notation, we note that in thermodynamics as well as in mechanics and electrodynamics, our equations are made cumbersome if we are forced to refer at all times to some particular coordinate system (i.e., set of independent variables). In the latter subjects this needless complication has long since been removed by the use of vector notation, which enables us to describe physical relationships without reference to any particular coordinate system. A similar house-cleaning can be effected for thermodynamics by use of jacobians, which enable us to express physical relationships without committing ourselves to any particular set of independent variables.

We have here an interesting example of retrograde progress in science: for the historical fact is that use of jacobians was the original mathematical method of thermodynamics. They were used extensively by the founder of modern thermodynamics, Rudolph Clausius, in his work dating from about 1850. He used the notation

$$D_{xy} \equiv \frac{\partial^2 Q}{\partial x \partial y} - \frac{\partial^2 Q}{\partial y \partial x} \qquad (2\text{-}2)$$

where Q stands, as always, for heat, and x, y are any two thermodynamic quantities. Since dQ is not an exact differential, D_{xy} is not identically zero. It is understandable that this notation, used in his published works, involved Clausius in many controversies, which in retrospect appear highly amusing. An account of some of them may be found in his book (Clausius, 1875). On the other hand, it is unfortunate that this occurred, because it is probably for this reason that the quantities D_{xy} went out of general use for many years, with only few exceptions (See comments at the end of this chapter). In a foot-

note in Chapter II of Planck's famous treatise (Planck, 1897), he explains that he avoids using dQ to represent an infinitesimal quantity of heat, because that would imply that it is the differential of some quantity Q. This in turn leads to the possibility of many fallacious arguments, all of which amount to setting $D_{xy} \equiv 0$. However, a reading of Clausius' works makes it clear that the quantities D_{xy}, when properly used, form the natural medium for discussion of thermodynamics. They enabled him to carry out certain derivations with a facility and directness which is conspicuously missing in most recent expositions. We leave it as an exercise for the reader to prove that D_{xy} is a jacobian (Problem 2.1).

We now develop a condensed notation in which the algebra of jacobians may be surveyed as a whole, in a form easy to remember since the abstract relations are just the ones with which we are familiar in connection with the properties of commutators in quantum mechanics.

2.2 Formal Properties of Jacobians

Consider first a system with only two degrees of freedom. We define

$$[A,B] \equiv \frac{\partial(A,B)}{\partial(x,y)} = \begin{vmatrix} \frac{\partial A}{\partial x} & \frac{\partial A}{\partial y} \\ \frac{\partial B}{\partial x} & \frac{\partial B}{\partial y} \end{vmatrix} \tag{2-3}$$

where x, y are any variables adequate to determine the state of the system. Since for a change of variables, $x, y \to x', y'$ we have

$$\frac{\partial(A,B)}{\partial(x',y')} = \frac{\partial(A,B)}{\partial(x,y)} \frac{\partial(x,y)}{\partial(x',y')} \tag{2-4}$$

or, in an easily understandable condensed notation,

$$[A,B]' = [A,B][x,y]' \tag{2-5}$$

It follows that any equations that are homogeneous in the jacobians are invariant in form under "coordinate transformations", so that we can suppress the independent variables x, y and carry out derivations without committing ourselves to any particular set.

The algebra of these symbols is characterized by the following identities (the comma may be omitted if A, B are single letters). The properties of antisymmetry, linearity, and composition have the familiar form

$$[AB] = - [BA], \qquad [AA] = 0 \tag{2-6}$$

$$[A \pm B,C] = [AC] \pm [BC] \tag{2-7}$$

$$[AB,C] = [AC]B + A[BC] \tag{2-8}$$

In addition we have three cyclic identities, easily proved:

$$[AB]\, dC + [BC]\, dA + [CA]\, dB = 0 \tag{2-9}$$

$$[A,[BC]] + [B,[CA]] + [C,[AB]] = 0 \tag{2-10}$$

$$[AB][CX] + [BC][AX] + [CA][BX] = 0 \tag{2-11}$$

The final fundamental property is the "theorem"

Let $dA = b\, dB + c\, dC.$ (2-12)

Then, for all X,

$$[AX] = b[BX] + c[CX]. \tag{2-13}$$

These relations are not all independent; for example, (2-11) follows from (2-9) and (2-13).

Putting dC = 0 in (2-9), we obtain the rule

$$\left(\frac{\partial A}{\partial B}\right)_C = \frac{[AC]}{[BC]} = \frac{[CA]}{[CB]} \tag{2-14}$$

by means of which equations are translated from one language to the other.

From it one sees that the transformation law (2-1) now appears as a special case of the identity (2-11). Writing for the enthalpy, free energy, and Gibbs function respectively,

$$\begin{aligned} H &= U + PV \\ F &= U - TS \\ G &= U - TS + PV \end{aligned} \tag{2-15}$$

where U is the internal energy with the property $dU = t\,dS - P\,dV$, we have as consequences of (2-13) the relations

$$\begin{aligned} [UX] &= T[SX] - P[VX] \\ [HX] &= T[SX] + V[PX] \\ [FX] &= -S[TX] - P[VX] \\ [GX] &= -S[TX] + V[PX] \end{aligned} \tag{2-16}$$

The advantages of this notation is shown particularly when we consider the four Maxwell equations

$$\left(\frac{\partial T}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial S}\right)_V \tag{2-17a}$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{2-17b}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \tag{2-17c}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \tag{2-17d}$$

Applying (2-14), we see that each reduces to the single identity

$$[TS] = [PV] \tag{2-18}$$

Thus, all of the Maxwell equations are expressions in different "coordinate systems" of the same basic fact (2-18), which will receive a physical interpretation in Sec. 2.4. In a derivation, such as that of Eq. (1-49), everything that can be gained by using any of the equations (2-17) is already accomplished by application of the single relation (2-18).

Jacobians which involve the entropy in combinations other than [TS] are related to various specific heats. The heat capacity at constant X is

$$C_X = T \left(\frac{\partial S}{\partial T}\right)_X \tag{2-19}$$

and, using (2-14) we obtain the identity

$$[SX] = \frac{C_X}{T} [TX] \tag{2-20}$$

In the simplest derivations, application of (2-18) or (2-20) is the essential step.

In his well-known textbook, Zemansky (1943) shows that many of the elementary derivations in thermodynamics may be reduced to application of the "T dS equations"

$$T\,dS = C_v\,dT + T \left(\frac{\partial P}{\partial T}\right)_V dV \tag{2-21}$$

$$T\,dS = C_p\,dt - T \left(\frac{\partial V}{\partial T}\right)_P dP \tag{2-22}$$

and the "energy equation",

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \tag{2-23}$$

In the above notation these equations are far from obvious and not easy to remember. Note, however, that the T dS equations are special cases of the cyclic identity (2-9) for the sets of variables {TVS}, {TPS}, respectively, while the energy equation is a consequence of (2-13) and the Maxwell relation:

$$[UT] = T[ST] - P[VT] = - T[PV] - P[VT] \tag{2-24}$$

From (2-14) we see that this is the energy equation in jacobian notation.

2.3 Elementary Examples

In a large class of problems, the objective is to express some quantity of interest, or some condition of interest, in terms of experimentally measurable quantities. Therefore, the "sense of direction" in derivations is provided by the principle that we want to get rid of any explicit appearance of the entropy and the various energies U, H, F, G. Thus, if the entropy appears in the combination [TS], we use the Maxwell relation to replace it with [PV]. If it appears in some other combination [SX], we can use the identity (2-20).

Similarly, if combinations such as [HX] or [UX] appear, we can use (2-16) and replace them with

$$[HX] = T[SX] + V[PX] = C_X[TX] + V[PX] \tag{2-25}$$

$$[UX] = C_X[TX] - P[VX] \tag{2-26}$$

If the entropy appears outside a jacobian, as in $[GX] = - S[TX] + V[PX]$, it cannot be eliminated in this way. However, since in phenomenological thermodynamics the absolute value of the entropy has no meaning, this situation cannot arise in any expression representing a definite physical quantity.

For problems of this simplest type, the jacobian formalism works like a well-oiled machine, as the following examples show. We denote the isothermal compressibility, thermal expansion coefficient, and ratio of specific heats by K, β, γ, respectively:

$$K = - \frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T = \frac{[TV]}{V[PT]} \tag{2-27}$$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{[PV]}{V[PT]} \tag{2-28}$$

$$\gamma = \frac{C_p}{C_v} \tag{2-29}$$

and note that from (2-27) and (2-28) we have

$$\frac{K}{\beta} = \frac{[TV]}{[PV]} = \left(\frac{\partial T}{\partial P}\right)_V \tag{2-30}$$

Several derivatives, chosen at random, are now evaluated in terms of these quantities:

$$\left(\frac{\partial U}{\partial P}\right)_S = \frac{[US]}{[PS]} = \frac{T[SS] - P[VS]}{[PS]} = -P\frac{C_v}{C_p}\frac{[TV]}{[TP]} = \frac{PVK}{\gamma} \tag{2-31}$$

$$\left(\frac{\partial U}{\partial T}\right)_S = \frac{[US]}{[TX]} = \frac{T[SS] - P[VS]}{[PV]} = P\frac{C_v}{T}\frac{[TV]}{[PV]} = \frac{PC_vK}{T\beta} \tag{2.32}$$

$$\left(\frac{\partial T}{\partial S}\right)_U = \frac{[TU]}{[SU]} = \frac{T[ST] - P[VT]}{T[SS] - P[VS]} = \frac{T}{P}\frac{T[VP] - P[VT]}{C_v[TV]} = \frac{T}{C_v}\left[1 - \frac{T\beta}{PK}\right] \tag{2-33}$$

$$\left(\frac{\partial H}{\partial V}\right)_P = \frac{[HP]}{[VP]} = \frac{T[SP] + V[PP]}{[VP]} = C_p\frac{[TP]}{[VP]} = \frac{C_p}{\beta V} \tag{2-34}$$

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{[TH]}{[PH]} = \frac{T[ST] + V[PT]}{T[SP] + V[PP]} = \frac{T[VP] + V[PT]}{C_p[TP]} = \frac{V}{C_p}(\beta T - 1) \tag{2-35}$$

$$\left(\frac{\partial F}{\partial S}\right)_T = \frac{[FT]}{[ST]} = \frac{-S[TT] - P[VT]}{[VP]} = -\frac{PK}{\beta} \tag{2-36}$$

$$\left(\frac{\partial G}{\partial V}\right)_T = \frac{[GT]}{[VT]} = \frac{-S[TT] + V[PT]}{[VT]} = -\frac{1}{K} \tag{2-37}$$

A more difficult type of problem is the following: We have given a number of quantities and wish to find the general relation, if any, connecting them. In one sense, the question whether relations exist can be answered

immediately; for any two quantities A, B a necessary and sufficient condition for the existence of a functional relation A = f(B) in a region R is: {[AB] = 0 in R}. In a system of two degrees of freedom it is clear that between any three quantities A, B, C there is necessarily at least one functional relation f(A,B,C) = 0, as is implied by the identity (2-9) [Problem 2.2]. An example is the equation of state f(PVT) = 0. This, however, is not the type of relation one usually has in mind. For each choice of A, B, C and each particular system of two degrees of freedom, some functional relationship must exist, but in general it will depend on the physical nature of the system and can be obtained only when one has sufficient information, obtained from measurement or theory, about the system.

The problem is rather to find those relations between various quantities which hold generally, regardless of the nature of the particular system. Mathematically, all such relations are trivial in the sense that they must be special cases of the basic identities already given. Their physical meaning may, however, be far from trivial and they may be difficult to find. Note, for example, that the derivative computed in (2-35) is just the Joule-Thomson coefficient μ. Suppose the problem had been stated as: "Given the five quantities $\{\mu, V, C_p, \beta, T\}$, determine whether there is a general relation between them and if so find it." Now, although a repetition of the argument of (2-35) would be successful in this case, this success must be viewed as a lucky accident from the standpoint of the problem just formulated. It is not a general rule for attacking this type of problem because there is no way of ensuring that the answer will come out in terms of the desired quantities.

To illustrate a general rule of procedure, consider the problem of finding a relationship, if any, between $\{C_p, C_v, V, T, \beta, K\}$. First we write these quantities in terms of jacobians.

$$C_p = T\frac{[SP]}{[TP]}, \qquad C_v = T\frac{[SV]}{[TV]}$$
$$\beta = \frac{[VP]}{V[TP]} \qquad K = \frac{[TV]}{V[PT]} \tag{2-38}$$

At this point we make a definite choice of some coordinate system. Since [TP] occurs more often than any other jacobian, we adopt x = T, y = P as the independent variables; thus [TP] $\equiv$ 1. We can now solve for the remaining jacobians:

$$[SP] = \frac{C_p}{T}, \qquad [VP] = \beta V$$
$$[VS] = \frac{C_v KV}{T}, \qquad [VT] = KV \tag{2-39}$$

The variables in jacobians are P, V, T, S, for which (2-11) gives

$$[PV][TS] + [VT][PS] + [TP][VS] = 0 \tag{2-40}$$

or, in this case

$$[PV]^2 + [VT][PS] + [VS] = 0. \tag{2-41}$$

Substituting the expressions (2-39) into this we obtain

$$\beta^2V^2 - KV\frac{C_p}{T} + \frac{C_v KV}{T} = 0$$

or, rearranging, we have the well-known law

$$C_p - C_v = \frac{TV\beta^2}{K} \tag{2-42}$$

which is now seen as a special case of (2-11).

There are several points to notice in this derivation: (1) no use has been made of the fact that the quantities T, V were given explicitly; the

argument supplied them automatically. (2) The solution depends in no way on the particular coordinate system adopted; if we had chosen [TV] = 1, the algebra would have been very slightly longer, with the same result. (3) The particular arrangement of (PVTS) in (2-40) has no influence on the result; after an arbitrary permutation of (PVTS), Eq. (2-40) still says exactly the same thing. (4) It was essential to the method that all the quantities be expressible in terms of jacobians of exactly four variables, but any four in place of PVTS would have served just as well.

In solid-state physics, C_V is most easily calculated from theory, while C_p is most easily measured in the laboratory. Equation (2-42) is therefore much used (often in approximate forms known as the Eucken-Grüneisen relation, or the Nernst-Lindemann equation) for the correction of experimental specific heat data before comparison with theory. For further details, see Zemansky (1943), Chap. 13; or Callen (1960), Appendix E.

As a second example, consider again the problem of the Joule-Thomson coefficient; find a relation between $\{\mu, \beta, C_p\}$ and any other quantities that may be needed. Proceeding as before, we have

$$\mu = \frac{[HT]}{[HP]} = \frac{T[ST] + V[PT]}{T[SP]}$$

$$\beta = \frac{[VP]}{V[TP]} \quad , \qquad C_p = T\frac{[SP]}{[TP]}$$

Choosing the coordinate system [SP] = 1, and solving for the remaining jacobians, we have

$$[TP] = \frac{T}{C_p}$$

$$[VP] = \frac{\beta VT}{C_p}$$

but at this stage we see already that the jacobians [TP], [VP] are the only ones appearing in μ, so we have immediately the result (2-35):

$$\mu = [VP] + \frac{V}{T}[PT] = \frac{\beta VT}{C_p} - \frac{V}{T}\frac{T}{C_p} = \frac{V}{C_p}(\beta T - 1) \qquad (2\text{-}43)$$

and the identity (2-11) was not needed.

As a third example consider the problem of finding a relation between β, K, C_p, and the quantity $\alpha = (\partial U/\partial T)_S$. The calculation goes through exactly as in the first example, with the result

$$\alpha = P\left[\frac{KC_p}{T} - \beta V\right] \quad . \qquad (2\text{-}44)$$

We have already found a simpler formula for α in (2-32). By use of (2-42) one shows that (2-44) and (2-32) are indeed equivalent. If we had chosen the variables $\{\alpha, \beta, K, C_v\}$ we would once again have found a "shortcut" that takes us directly to (2-32) without use of (2-11).

In the first type of problem, illustrated by equations (2-30) through (2-37), we are content to find the quantity or condition of interest in terms of <u>any</u> experimentally measurable quantities. After finding any such relationship, one can apply the basic identities and transform it into various other forms. In the second type of problem we demand that the result must come out in terms of certain <u>specified</u> quantities, for example the ones which we have measured. The second method of procedure leads us directly to this relation if it exists.

As a final example, suppose we have measured C_p and the thermal expansion coefficient β at various temperatures and volumes. Are these data sufficient to determine the quantity $\delta \equiv (\partial T/\partial P)_U$? If not, what additional measurements must we make? In the coordinate system [SP] = 1, we find the relations

$$[TP] = \frac{T}{C_p} \quad , \qquad [VP] = \frac{\beta VT}{C_p}$$

$$[VT] = \frac{T}{P}\left[\frac{\beta VT}{C_p} - \delta\right]$$

and substituting into (2-40) we have

$$[SV] = \frac{\beta^2 V^2 T}{C_p} + \frac{C_p}{P} - \frac{\beta VT}{P} \, . \tag{2-45}$$

We do not yet have the desired result because there is nothing which determines the jacobian [SV]. This means that β and C_p are not enough to determine δ; but we can determine the missing quantity as follows. The extra jacobian (2-45) is, from (2-20),

$$[SV] = \frac{C_v}{T}[TV] = \frac{C_v}{P}\left[\delta - \frac{\beta VT}{C_p}\right] \tag{2-46}$$

Thus, it would be sufficient to measure also C_v. Equating (2-45) and (2-46) and solving for δ,

$$\delta = \frac{\beta VT}{C_p}\left[1 - \frac{\beta VP}{C_p - C_v}\right] \tag{2-47}$$

which, using (2-42), may also be written as

$$\delta = \frac{V}{C_p}(\beta T - KP). \tag{2-48}$$

so that a measurement of the compressibility K would also suffice.

It is impossible to appreciate the ease with which these derivations have been carried out here unless one also tries to derive them without making any use of jacobians; the reader is urged to do this for himself [Problem

2.4 Physical Meaning of Jacobians

The preceding discussion, while demonstrating the power and usefulness of jacobians in thermodynamics, has raised more questions than it has answered. What do the jacobians mean? Why do these methods work so well? Can we find a point of view which makes it clear from the start that jacobians rather than partial derivatives are the "natural" quantities of thermodynamics? And a much deeper question: Why is it that in so many different branches of physics, the introduction of antisymmetric bracket symbols, all with the same abstract algebraic properties, leads to the most succinct and powerful methods of calculation?

As a start toward answering these questions we observe that, in spite of first appearances, jacobians are actually simpler quantities than are partial derivatives. Because of the fact that the particular coordinate system x, y is unimportant, we can regard a jacobian as expressing a mutual property of two variables, while a partial derivative represents a joint property of three variables. One interpretation of this mutual property follows from the familiar use of jacobians in transforming an element of volume in multiple integrals. Thus, consider a quantity Z(x,y) which is a function of state of the system, and a certain range of states represented by the area r in the (x-y) plane. In terms of a different set of variables A, B this same set of states is mapped onto a corresponding region R in the (A-B) plane. Then the integral of Z over this region is given by

$$\int_R Z \, dA \, dB = \int_r Z \, \frac{\partial(A,B)}{\partial(x,y)} \, dx \, dy \tag{2-49}$$

Thus elements of volume corresponding to the same range of states transform according to

$$dR = \frac{\partial(A,B)}{\partial(x,y)} \, dr \tag{2-50}$$

or, the jacobian is the local magnification factor in the mapping of the (x-y) plane onto the (A-B) plane.

These remarks are illustrated in Fig. 2.1, in which we see an infinitesimal Carnot cycle as viewed in the six different planes which can be formed from the coordinates P, V, T, S. Adopting the convention that the rectangle in the T-S plane encloses unit area, the jacobian [AB] is then equal to the area enclosed by the mapping of this Carnot cycle onto the A-B plane, with a positive sign if it is described in a counterclockwise direction, negative if clockwise. The Maxwell equation (2-17a) is often described as expressing the fact that (T dS - P dV) is an exact differential; an equivalent statement which has perhaps more intuitive appeal is that the mapping of the T-S plane onto the P-V plane always preserves areas. This is just the statement that the work done in a closed reversible cycle can be found equally well from the T-S diagram as the P-V diagram: $\oint T\, dS = \oint P\, dV$.

The content of the identity (2-11):

$$[PV][TS] + [VT][PS] + [TP][VS] = 0$$

is that, given the ratios [TS]:[PS]:[VS] of the areas of the top three diagrams, one linear combination of the areas [PV], [VT], [TP] is determined. A study of Fig. 2.1 discloses the geometrical reason for this and shows that a stronger statement can be made: Given the top three diagrams, all the others may be constructed by projections as shown.

The interpretation of a jacobian [AB] as giving the area and direction of travel for an infinitesimal reversible cycle, as seen in the A-B plane, is probably the most convenient one. However, another way of looking at it is to draw in the x-y plane the contours A(x,y) = const., B(x,y) = const., as in Fig. 2.2. If we imagine a z-axis at right angles to the paper, we see that the jacobian can be written as a vector cross-product

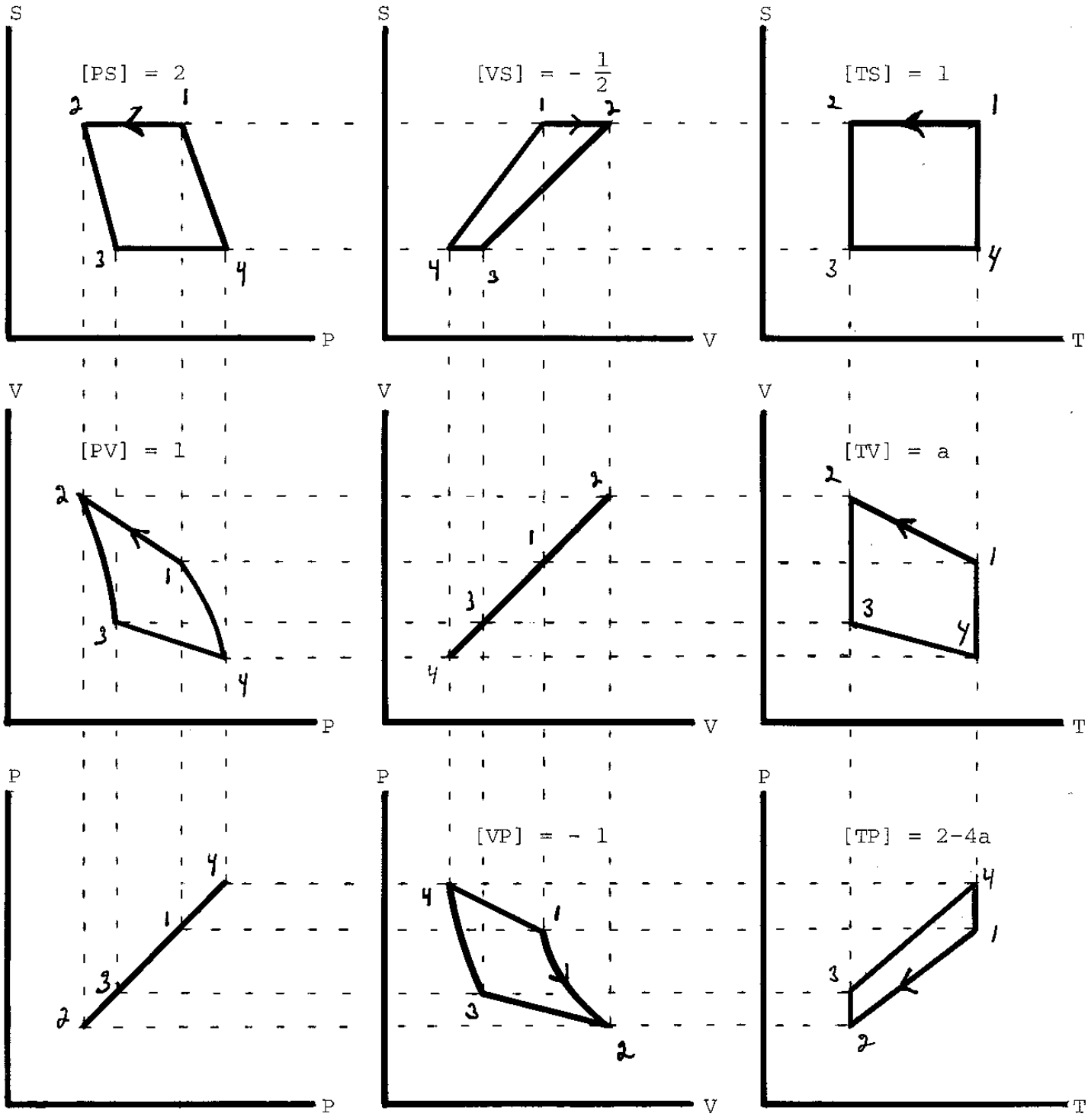

Figure 2.1. An infinitesimal Carnot cycle as seen in several coordinate planes.

1 → 2 adiabatic expansion

2 → 3 isothermal compression

3 → 4 adiabatic compression

4 → 1 isothermal expansion

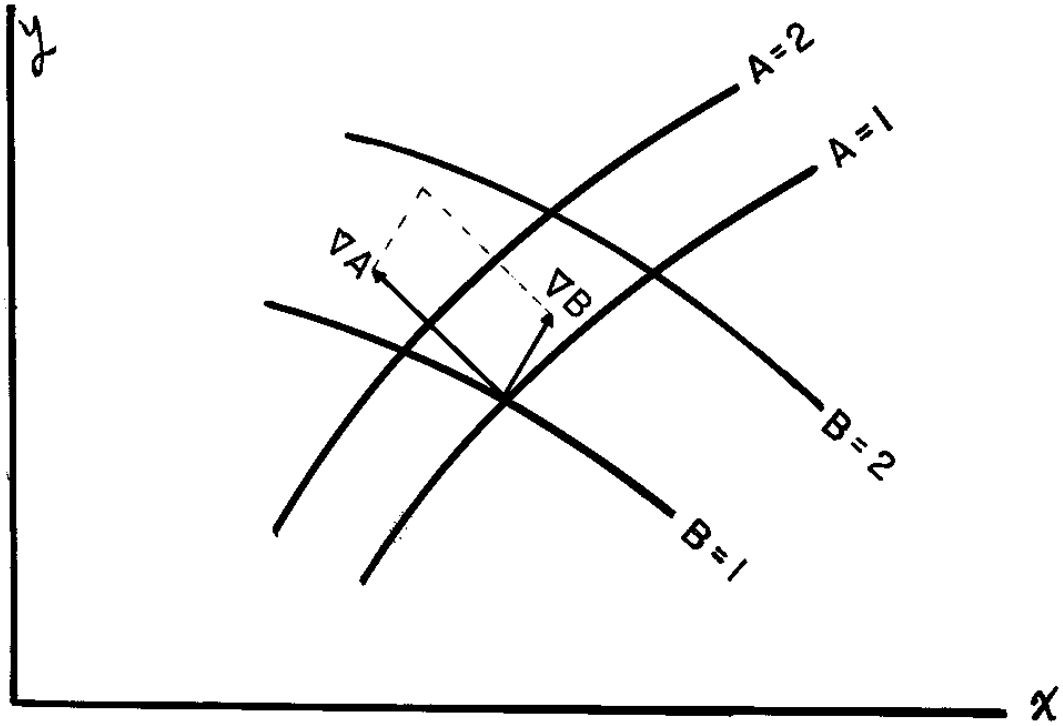

Figure 2.2. Lines of constant A and constant B in the x-y plane. The jacobian [A,B] is equal to the area of the parallelogram.

$$\frac{\partial(A,B)}{\partial(x,y)} = \frac{\partial A}{\partial x}\frac{\partial B}{\partial y} - \frac{\partial A}{\partial y}\frac{\partial B}{\partial x} = (\nabla A \times \nabla B)_z \qquad (2\text{-}51)$$

of the gradients $\vec{\nabla}A$, $\vec{\nabla}B$. Its numerical value is therefore equal to the area of the parallelogram whose sides are $\vec{\nabla}A$, $\vec{\nabla}B$. At any point where [A,B] = 0, the lines B = const., A = const., are tangent to each other. At such a point, any infinitesimal change of state which holds A constant also holds B constant; thus, the condition for the inversion point of the Joule-Thompson effect is

$$0 = [HT] = T[ST] + V[PT] = T[VP] + V[PT] \qquad (2\text{-}52)$$

This appears as a singular point in the mapping of the P-V plane onto the H-T plane.