

Jacobian Methods in Thermodynamics

F. H. Crawford

Citation: *Am. J. Phys.* **17**, 1 (1949); doi: 10.1119/1.1989489

View online: <http://dx.doi.org/10.1119/1.1989489>

View Table of Contents: <http://ajp.aapt.org/resource/1/AJPIAS/v17/i1>

Published by the American Association of Physics Teachers

Additional information on Am. J. Phys.

Journal Homepage: <http://ajp.aapt.org/>

Journal Information: http://ajp.aapt.org/about/about_the_journal

Top downloads: http://ajp.aapt.org/most_downloaded

Information for Authors: <http://ajp.dickinson.edu/Contributors/contGenInfo.html>

ADVERTISEMENT



WebAssign®

The PREFERRED Online Homework Solution for Physics

Every textbook publisher agrees! Whichever physics text you're using, we have the proven online homework solution you need. WebAssign supports every major physics textbook from every major publisher.

webassign.net

Logos on laptop screen: CENGAGE Learning, WILEY, openstax COLLEGE, W.H. FREEMAN, Physics Curriculum & Instruction, McGraw Hill Higher Education, PEARSON

AMERICAN JOURNAL of PHYSICS

A Journal Devoted to the Instructional and Cultural Aspects of Physical Science

VOLUME 17, NUMBER 1

JANUARY, 1949

Jacobian Methods in Thermodynamics

F. H. CRAWFORD

Williams College, Williamstown, Massachusetts

I.

THE usefulness of Jacobians, or functional determinants, in general thermodynamic discussions has not received the emphasis which the power and directness of Jacobian methods warrant. Thus one of the important problems in developing the subject is that of obtaining the so-called "general relations" of thermodynamics. The most important group of these involves the determination of all of those relations involving *first* partial derivatives which must obtain in consequence of the two laws of thermodynamics and certain general and fundamental mathematical theorems. Since it can be shown that for a given physical system any desired derivative can be expressed in terms of an irreducible standard set of first derivatives, the problem becomes that of evolving the most expeditious method for expressing any derivative directly in terms of this standard set. It can be shown that for a general n -variable system (with no special restrictions) this set contains $n(n+1)/2$ derivatives.¹ For a simple homogeneous system under hydrostatic pressure, which we shall have in mind during most of the present discussion, $n=2$, and this standard set contains three *partial derivatives*.

To be more specific we may, after Clausius, express the first and second laws in a combined

form as

$$dU = TdS - pdV, \quad (1)$$

where U is the internal energy of the system, S the entropy, and the other symbols have their usual meanings. Our problem, then, is to express any given partial derivative in terms of a standard set by the use of such general mathematical theorems as are available and subject, of course, to Eq. (1). Now these results may be obtained in a great variety of ways, and, in fact, for the system in question are given in a complete form by Bridgman.² The usual methods of obtaining these relations are, however, roundabout and tedious, and involve rather cumbersome eliminations. The utility of Jacobians or functional determinants in such cases has received altogether too little attention, despite the fact that Jacobians seem particularly suited for the concise statement of the complex of relationships involved. Several of the older books on thermodynamics³ express certain derivatives in terms of Jacobians but do not carry the discussion quite far enough for the very real practical advantages to become apparent. More recently, Shaw⁴ has given an extremely elegant and elaborate discussion of the hydrostatic case. The fundamental Jacobian theorems used there, however, are of such a form

² P. W. Bridgman, *A condensed collection of thermodynamic formulas* (Harvard University Press, 1925), pp. 10–15.

³ See, for example, Bryan, *Thermodynamics* (Leipzig, 1907), p. 22, *et seq.*

¹ F. H. Crawford, *Physical Rev.* **72**, 521A (1947). The general results of the n -variable case will be given in more detail elsewhere.

⁴ A. N. Shaw, *Phil. Trans. Roy. Soc.* **A234**, 299–378 (1935).

as to require considerable dexterity in their manipulation and continual refreshing of one's memory unless they are being used continually.

The method to be discussed here is essentially a special case of Shaw's method but has the practical advantages of being very simple to remember, of needing only *one* intermediate equation obtainable quickly from Eq. (1), and of being capable of ready generalization to systems with $n > 2$. There are three steps involved, of which the first two employ Jacobians. They depend for their ease and directness on the use of certain simple and well-known properties of Jacobians. These will be summarized here without proof, though the proofs are simple.⁵

II. Useful Properties of Jacobians

Let us consider, for example, the Jacobians of entropy and volume with respect to the independent variables, x and y . Then we have

$$J(S, V) = \partial(S, V)/\partial(x, y) = \begin{vmatrix} (\partial S/\partial x)_y & (\partial V/\partial x)_y \\ (\partial S/\partial y)_x & (\partial V/\partial y)_x \end{vmatrix}, \quad (2)$$

where the notation $J(S, V)$ will be used wherever the independent variable set is clearly apparent.

(a) *Reduction of Jacobians to single derivatives:* Whenever the numerator and denominator of a Jacobian contains a common variable this may formally be "canceled," thus reducing a second-order Jacobian to a single derivative. The canceled variable appears outside the bracket of the partial derivative. Thus,

$$\partial(S, V)/\partial(S, y) = (\partial V/\partial y)_s.$$

Cross cancellation always involves a change in sign. Thus

$$\partial(S, V)/\partial(x, S) = -(\partial V/\partial x)_s.$$

Conversely, of course, we may "expand" any first derivative into a second-order Jacobian.

(b) *Change of order of variables* alters the sign of a Jacobian. Thus

$$J(S, V) = -J(V, S) = \partial(V, S)/\partial(y, x), \text{ etc.}$$

(c) *A Jacobian does not vanish* unless a functional relation exists between its dependent

variables. Thus $J(S, V) \neq 0$ unless $S = S(V)$, which is not true in our homogeneous system of two degrees of freedom. Hence we may divide by and cancel such Jacobians algebraically without ambiguity.

(d) *Change of variable theorem:* If, for example, each of the set (S, V) is a function of (x, y) and each of these in turn is a function of a new set (X, Y) , then

$$\partial(S, V)/\partial(X, Y) = \frac{(\partial(S, V)/\partial(x, y))}{(\partial(X, Y)/\partial(x, y))}. \quad (3)$$

This is the most general change of variable theorem, and includes as special cases the most useful theorems in partial differentiation. (We shall refer to it in the sequel simply as the Jacobian theorem.)

III. General Method for Obtaining Relations

(a) *Step one: Expression of a derivative in terms of no more than four others.* This step consists in expanding any derivative into a Jacobian and then applying the Jacobian theorem, Eq. (3) above. As an example consider $(\partial S/\partial p)_v$. We may write at once

$$\begin{aligned} (\partial S/\partial p)_v &= \partial(S, V)/\partial(p, V) \\ &= \frac{(\partial(S, V)/\partial(x, y))}{(\partial(p, V)/\partial(x, y))} = J(S, V)/J(p, V). \end{aligned} \quad (4)$$

Now $J(S, V)$ contains four derivatives and $J(p, V)$ two new ones, or six all told. These will in all cases reduce to no more than *four*, however, provided x and y are selected from the set (T, S, p, v) only, since at least one derivative will always vanish and another reduce to unity. Hence, in Eq. (4) we have expressed a partial derivative in terms of the ratio of two independently calculable Jacobians which *at most* can involve four distinct first derivatives. This step, of course, is a purely mathematical transformation and holds whether or not our symbols have any reference to a physical system or not.

(b) *Step two: Deduction of Maxwell's equation in Jacobian form.*⁶ We must now use some aspect of

⁵ See, for example, Margenau and Murphy, *The mathematics of physics and chemistry* (Van Nostrand, 1943), p. 18.

⁶ This extremely concise and useful theorem is given by Saha and Srivastava, *A text book of heat* (Allahabad, 1931), p. 408, *et seq.* The above proof is, I believe, new.

the truth contained in the laws of thermodynamics as expressed in Eq. (1),

$$dU = TdS - pdV.$$

The most pertinent way to do this is to utilize the fact the dU is a *perfect* or *total differential* and apply the cross derivative theorem to $TdS - pdV$. This gives us

$$(\partial T/\partial V)_S = -(\partial p/\partial S)_V, \quad (5)$$

which, although a true relation, is in terms of (S, V) as independent variables. To express it in its most general form in terms of, say, (x, y) , we have simply to apply the method of step one to each side of Eq. (5). This gives us for the left side

$$\begin{aligned} (\partial T/\partial V)_S &= \partial(T, S)/\partial(V, S) \\ &= \frac{(\partial(T, S)/\partial(x, y))}{(\partial(V, S)/\partial(x, y))} = J(T, S)/J(V, S), \end{aligned}$$

and for the right side

$$\begin{aligned} -(\partial p/\partial S)_V &= -\partial(p, V)/\partial(S, V) = \partial(p, V)/\partial(V, S) \\ &= \frac{(\partial(p, V)/\partial(x, y))}{(\partial(V, S)/\partial(x, y))} = J(p, V)/J(V, S). \end{aligned}$$

Hence Eq. (5) becomes

$$J(T, S)/J(V, S) = J(p, V)/J(V, S)$$

or, since $J(V, S) \neq 0$, we may cancel this Jacobian out of our result and obtain, finally,

$$J(T, S) = J(p, V),$$

or

$$(\partial(T, S)/\partial(x, y)) - (\partial(p, V)/\partial(x, y)) = 0. \quad (6)$$

This, then, is the general Jacobian relation whose special forms are usually known as Maxwell's relations. Since there are six choices of variable sets, if we confine ourselves to (T, S, p, V) , we have six forms of Eq. (6). These are not six independent equations but merely six equivalent ways of writing Eq. (5). We may then refer to the appropriate form of Eq. (6) simply as Maxwell's relation.

It is important to note that when (x, y) is a *non-conjugate* set such as (S, V) , (T, p) , etc., Maxwell's relation always reduces to two derivatives. If we choose a conjugate set, either (T, S) or (p, V) , we have an expression involving four

derivatives. In all cases, however, no new derivatives appear beyond those arising in step one.

(c) *Step three: Combination of results of steps one and two.* We are now in a position to obtain the final result. By step one we have written a given derivative in terms of no more than four other derivatives. From step two we obtain a relation involving two or more of this same group. Hence we may eliminate one of the four derivatives and *express our desired derivative in terms of a standard set of three partial derivatives of the dependent variables with respect to x and y* , provided, of course, that both dependent and independent variables are selected from the set (T, S, p, V) .

IV. Specific Examples in Simple Hydrostatic Case

In the above discussion we have left the choice of x and y open. In practice it is convenient to take T and p since they are readily controlled experimentally. To find a given derivative such as $(\partial S/\partial p)_V$ from above, we have, using step one by applying Eq. (4),

$$\begin{aligned} (\partial S/\partial p)_V &= \partial(S, V)/\partial(p, V) \\ &= (\partial(S, V)/\partial(T, p))/(\partial(p, V)/\partial(T, p)) \\ &= \frac{\begin{vmatrix} (\partial S/\partial T)_p & (\partial V/\partial T)_p \\ (\partial S/\partial p)_T & (\partial V/\partial p)_T \end{vmatrix}}{-(\partial V/\partial T)_p} = \frac{\begin{vmatrix} a & b \\ d & c \end{vmatrix}}{-b}, \quad (7) \end{aligned}$$

where the letters a, b, c and d are simply abbreviations for the four derivatives in $J(S, V)$.

Now by step two, Eq. (6), we obtain Maxwell's relation in the form

$$\partial(T, S)/\partial(T, p) - \partial(p, V)/\partial(T, p) = 0,$$

or

$$(\partial S/\partial p)_T = -(\partial V/\partial T)_p, \text{ or simply } d = -b. \quad (8)$$

Since, then, b is more readily measured experimentally than d , we now use Eq. (8) to eliminate d from Eq. (7) and have as our final result:

$$(\partial S/\partial p)_V = (b^2 + ac)/-b.$$

We may now expect to determine all other derivatives which involve only (T, S, p, V) in

terms of the standard set a , b , and c ,⁷ though in a given case the whole set need not appear. Thus for $(\partial S/\partial V)_p$ we have

$$\begin{aligned} (\partial S/\partial V)_p &= \frac{(\partial(S, p)/\partial(T, p))}{(\partial(V, p)/\partial(T, p))} \\ &= \frac{(\partial S/\partial T)_p}{(\partial V/\partial T)_p} = a/b, \text{ etc.} \end{aligned}$$

Further, the method is entirely foolproof and, if we apply step one to any of the set a , b , c or d , we obtain simply an identity.

V. Extension to Other Quantities than the Primary Set (T, S, p, V)

We may now remove the earlier restriction to variables of the primary set. There are a number of quantities of special interest which are defined either differentially or integrally in terms of the primary set. These we group in a *secondary* set which will include, among others, the internal energy U , the enthalpy $H(=U+pV)$, the Helmholtz function $A(=U-TS)$, and Gibbs' function $G(=U-TS+pV)$. Consider, then, any derivative such as $(\partial X/\partial Y)_Z$, where X , Y and Z are chosen in any way whatever from these two sets. By step one, $(\partial X/\partial Y)_Z = J(X, Z)/J(Y, Z)$, and will contain only partials with respect to T and p . But these in turn are all expressible in terms of a , b , c and d and hence of a , b and c . The expressions may involve T , S , p and V themselves, but will never involve any derivatives not in the standard set of three. As an example, consider $(\partial U/\partial H)_T$. We have

$$\begin{aligned} (\partial U/\partial H)_T &= J(U, T)/J(H, T) \\ &= \frac{(\partial(U, T)/\partial(T, p))}{(\partial(H, T)/\partial(T, p))} = \frac{(\partial U/\partial p)_T}{(\partial H/\partial p)_T}. \end{aligned}$$

But $(\partial U/\partial p)_T$ we obtain from Eq. (1) and $(\partial H/\partial p)_T$ from the definition of H (and Eq. (1), again). Thus we have, finally,

$$(\partial U/\partial H)_T = bT + cp/bT - V.$$

⁷ Here, of course, $aT = C_p$, $bV = \beta_p$ and $cV = -K_T$, where C_p , β_p and K_T are, respectively, the heat capacity at constant pressure, the coefficient of volume expansion at constant pressure and the isothermal coefficient of compressibility. Their values may be got directly from tables of physical constants.

Now although Q and W , the heat absorbed by and the work done on the system, respectively, are not functions of the independent variables (T, p) , we may include them formally in the secondary set on the following understanding. Derivatives such as $(\partial X/\partial Y)_W$ are identical with $(\partial X/\partial Y)_V$, and $(\partial X/\partial Y)_Q$ is the equivalent of $(\partial X/\partial Y)_S$ since no heat is absorbed along an adiabatic. We also replace $(\partial Q/\partial X)_Z$ wherever it occurs formally, by dQ_Z/dX , where Q_Z is the heat function at constant Z . Similarly, $(\partial W/\partial X)_Z$ is to be taken as dW_Z/dX , where W_Z is the work function at constant Z .

If we then add Q and W to our set of primary and secondary quantities, we have ten all told, $T, S, p, V, U, H, A, G, Q$ and W . Any derivative will be expressible as the ratio of two Jacobians $J(X, Z)$ and $J(Y, Z)$. Hence all the conceivable derivatives can be formed if we compute all the Jacobians involving these ten quantities two at a time. There are $10 \times 9 = 90$ of these, of which 45 only need be computed since $J(X, Z) = -J(Z, X)$. This establishes the essential mathematical basis behind the tables of Bridgman;² he has precisely 90 such entries, and the quantities to be divided to give a desired derivative are simply our Jacobians. In his notation $(\partial X)_Z \equiv J(X, Z)$, $(\partial Y)_Z \equiv J(Y, Z) = \partial(Y, Z)/\partial(T, p)$, etc. Furthermore, we may now compute any entry in the table with Maxwell's relation and the definitions of any secondary quantities needed as our only intermediate equations.

VI. Other Systems

(a) *General systems.* The above process need not be confined to the simple hydrostatic system. We may replace Eq. (1) by

$$dU = TdS + Xd\theta, \quad (9)$$

where X is a force variable and θ the conjugate geometric variable. Here, as long as any two of the primary set (T, S, X, θ) may be regarded as the independent variables, we may express any derivative in terms of an appropriate standard set of three.

(b) *Restricted systems.* There are many systems to which Eq. (9) applies which are *restricted* in the sense that, for example, X may be a function of, say, T alone. In such cases we may not take

(T, X) as our independent variables but must use another pair such as (T, θ) .

Under these conditions the four derivatives which will turn up in step one are always to be found, formally at least, in $J(S, X)$, for S and X are now the dependent variables. But this gives us

$$\begin{aligned} J(S, X) &= \partial(S, X)/\partial(T, \theta) \\ &= \begin{vmatrix} (\partial S/\partial T)_\theta & (\partial X/\partial T)_\theta \\ (\partial S/\partial \theta)_T & (\partial X/\partial \theta)_T \end{vmatrix} \\ &= \begin{vmatrix} (\partial S/\partial T)_\theta & dX/dT \\ -dX/dT & 0 \end{vmatrix}, \end{aligned}$$

since the derivative $(\partial X/\partial \theta)_T = 0$ and Maxwell's relation reduces to $(\partial S/\partial \theta)_T = -dX/dT$. Consequently, we have only *two* independent first derivatives rather than the three of the general case.

The most important example of this restricted case is, of course, that of the two phases of a pure substance under pressure, where p , the equilibrium pressure, is $p(T)$. Other cases are a surface film under tension where the surface tension is a function of T alone, and a simple reversible electric cell (no gas evolution) where the electromotive force depends on T alone. In all such restricted systems we have as many formal Jacobians as in the general case, but they are all simpler.⁸

In practice it is usually quicker and more accurate to determine the desired derivative directly from the appropriate form of Eq. (9) than to calculate the corresponding result for the general hydrostatic case and then to translate the result for the new system.

⁸ See reference 2, pp. 18-24.

A Geometrical Introduction to Tensor Analysis for the Physicist

M. J. WALKER

The Pennsylvania State College, State College, Pennsylvania

THE operations of tensor analysis are not easy to visualize geometrically. This fact is of small concern to the analyst, but is a source of difficulty to most of those who approach tensor analysis for the first time. In particular, the physicist who finds only occasional use for tensor methods is likely to feel the need of a geometrical mnemonic aid for tensor concepts. Furthermore, there are students who feel dissatisfied with their understanding of a concept unless it can be visualized.

This paper shows how many of the concepts of tensor analysis may be visualized geometrically as generalizations of the concepts of vector analysis. The presentation is intended to supplement the analytical development of tensor theory, and therefore makes no pretense of proving anything. The general formulas and concepts of tensor analysis are reduced to the simplest usable special case, and this special case is illustrated geometrically. The general formulas are shown for comparison with the special case formulas. Also, the vocabulary of tensor analysis is retained for the special case of tensors of rank one—that

is, vectors—where vector terminology would be more usual.

The subject is developed synthetically, and certain *definitions* are introduced. These definitions are designed for the special case under consideration, and although they will be consistent with the general case, they are not intended to replace the rigorous definitions of the analytical development. Furthermore, it must be emphasized that a geometrical model, like any other analogy, has limitations; the model may have properties that the prototype analytical expression does not have, and conversely.

If one sets out to generalize vector analysis, three possibilities come immediately to the mind:

- a. The coordinate axes, along which the components are taken, may intersect at some angle θ , where θ is not 90° as in ordinary vector analysis.
- b. The unit of length along the coordinate axes may be different for each axis.
- c. The unit of length may vary in size as one proceeds along the axes.