

On the Use of Jacobians in Thermodynamics

It was interesting to see that the use of Jacobians in thermodynamics was demonstrated in a recent issue of THIS JOURNAL (1) without having to resort to the Shaw (2) procedure. Shortly thereafter another article (3) appeared suggesting that the student could be relieved of any knowledge of Jacobians by using a procedure described by Tobolsky some years ago. As one who recommended the Tobolsky procedure with some minor modifications in THIS JOURNAL (4) and has used it in the classroom for a number of years I would like to suggest that a few general properties of Jacobians and some features of the Tobolsky method may be combined in thermodynamic derivations to yield a direct, simple, and rapid method. Having used this combination in elementary thermodynamics, our experience has been that the students soon take to the use of Jacobians as ducks to water. A description of this procedure may encourage more widespread use of that extremely useful mathematical tool. The few rules required for the manipulation of Jacobians in the method discussed here are almost trivial.

The serious student will find the use of functional determinants advantageous in wading through mathematical hardware not only in relationships among the usual thermodynamic first partials for simple systems but also for systems where more than two independent variables are required. Jacobians may be used to great advantage in examining the higher order terms involved in equilibria (5); and of course there are many instances where Jacobians are used in allied branches of physical chemistry.

There is general agreement that a procedure for deriving relations among the thermodynamic derivatives without resorting to the Bridgman tables is highly desirable. The use of Jacobians makes for directness and speed. The work of Crawford (6) has done much to clarify and simplify the use of Jacobians in thermodynamics. The procedure based on the Tobolsky method can be made considerably less tedious. A few of the most common Jacobian properties are the only additional requirements.

The fundamental equations for the differential expressions of the so-called secondary variables (i.e., dE , dH , dA and dG) are still required, as well as the expressions for C_v and C_p . For a simple system four Maxwell equations are needed. The recommended procedure for obtaining the relation for a first partial in terms of a set of selected independent variables consists of the following three steps:

Step 1. Write the given partial immediately in terms of the selected independent variables.

Step 2. Replace the partials containing secondary variable by means of equations (1) through (4):

$$dE = TdS - PdV \quad (1)$$

$$dH = TdS + VdP \quad (2)$$

$$dA = -SdT - PdV \quad (3)$$

$$dG = -SdT + VdP \quad (4)$$

Step 3. Replace the partials containing the entropy variable by means of the Maxwell equations (which now may be written in Jacobian form as a single equation 5),

$$J(T,S) = J(P,V) \quad (5)$$

and also
$$\frac{C_v}{T} = \left(\frac{\partial S}{\partial V}\right)_v \quad (6a)$$

$$\frac{C_p}{T} = \left(\frac{\partial S}{\partial T}\right)_p \quad (6b)$$

Step 1: The expansion of a partial in terms of a set of selected independent variables.

It has been repeatedly shown (7) that a thermodynamic partial derivative may be written as a Jacobian, e.g.,

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{\partial(T,H)}{\partial(P,H)}$$

It should be noted that this is a reversible procedure; a Jacobian having a common variable in the numerator and denominator may be written as a simple partial derivative. When a common variable does not appear directly over itself the determinantal property of a Jacobian requires a change of sign, i.e.,

$$\frac{\partial(T,H)}{\partial(H,P)} = -\left(\frac{\partial T}{\partial P}\right)_H$$

Now if a change to a new set of independent variables (x,y) is desired, then these may be introduced into a Jacobian as follows:

$$\frac{\partial(T,H)}{\partial(P,H)} = \frac{\zeta(T,H)}{\frac{\partial(x,y)}{\partial(P,H)}}$$

where, e.g., the numerator

$$\frac{\partial(T,H)}{\partial(x,y)} = \begin{vmatrix} \left(\frac{\partial T}{\partial x}\right)_y & \left(\frac{\partial H}{\partial x}\right)_y \\ \left(\frac{\partial T}{\partial y}\right)_x & \left(\frac{\partial H}{\partial y}\right)_x \end{vmatrix}$$

We thus express a Jacobian as a ratio of *two* Jacobians in the transformation to a new set of independent variables. Consider an actual problem: the transformation of the Joule-Thomson coefficient, $(\partial T/\partial P)_H$ to the independent variables T and P . We write

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{\partial(T,H)}{\partial(P,H)} = \frac{\partial(T,H)}{\partial(T,R)} \frac{\partial(T,R)}{\partial(P,H)} = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P}$$

Whereas in the earlier procedure (4) one expressed a partial derivative in the form of a differential equation, the partial derivative in question is now expanded into a functional determinant and the selected independent variables are immediately introduced—yielding in general a ratio of two Jacobians. Were it not for the desirability of ridding the final expression of the so-called secondary variables, E, H, A, G and the entropy variable, the sought result would be contained in the very first step.

Step 2: The elimination of secondary variables, E, H, A, G .

This can be done on sight using the set of equations (1-4). We proceed with the problem of the Joule-Thomson coefficient and substitute the following in the last equation.

$$\begin{aligned} \left(\frac{\partial H}{\partial P}\right)_T &= T\left(\frac{\partial S}{\partial P}\right)_T + V \\ \left(\frac{\partial H}{\partial T}\right)_P &= T\left(\frac{\partial S}{\partial T}\right)_P \end{aligned}$$

These expressions of course are directly obtainable from equation (2) and obviously should be modified in accordance with Step 3 before they are substituted in the main equation.

Step 3: The elimination of the entropy variable.

This step will be recognized as one that is precisely the same as in the previous method (4) except that the procedure now can be somewhat more elegant. To continue with the Joule-Thomson example we use equation (5) and write immediately the desired Maxwell equation.

$$\begin{aligned} \frac{\partial(T, S)}{\partial(T, P)} &= \frac{\partial(R, V)}{\partial(T, R)} \\ \left(\frac{\partial S}{\partial P}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_P \end{aligned}$$

Note that the order of the selected independent variables must be preserved. Substitution of the latter equation and the expression for $(\partial S/\partial T)_P$ using equation (6b) leads to the well known equation for the Joule-Thomson coefficient in terms of the independent variables, T and P :

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T}\right)_P - V \right]$$

Many times students will recognize certain partials and use shortcuts; in the above example $(\partial H/\partial T)_P$ would be recognized as C_p . However the three-step procedure is direct and systematic.

As another example for using this procedure, we take the one illustrated by both Hakala and Breen: the equation for $(\partial E/\partial V)_H$ in terms of the independent variables T and P . We have:

Step 1.

$$\left(\frac{\partial E}{\partial V}\right)_H = \frac{\partial(E, H)}{\partial(T, P)} = \frac{\left(\frac{\partial E}{\partial T}\right)_P \left(\frac{\partial H}{\partial P}\right)_T - \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial E}{\partial P}\right)_T}{\frac{\partial(V, H)}{\partial(T, P)} = \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial H}{\partial P}\right)_T - \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial V}{\partial P}\right)_T}$$

Step 2. We need expressions for the following:

$$\begin{aligned} \left(\frac{\partial E}{\partial T}\right)_P &= T \left(\frac{\partial S}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial T}\right)_P \\ \left(\frac{\partial E}{\partial P}\right)_T &= T \left(\frac{\partial S}{\partial P}\right)_T - P \left(\frac{\partial V}{\partial P}\right)_T \\ \left(\frac{\partial H}{\partial P}\right)_T &= T \left(\frac{\partial S}{\partial P}\right)_T + V \\ \left(\frac{\partial H}{\partial T}\right)_P &= T \left(\frac{\partial S}{\partial T}\right)_P \end{aligned}$$

Step 3. We also need the following expressions in view of the entropy partials in Step 2.

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

Also from equation (6b)

$$T \left(\frac{\partial S}{\partial T}\right)_P = C_p$$

Direct substitution of the required partials in the equation for Step (1) yields

$$\left(\frac{\partial E}{\partial V}\right)_H = \frac{-VC_p}{C_p \left(\frac{\partial V}{\partial P}\right)_T + T \left(\frac{\partial V}{\partial T}\right)_P^2 - V \left(\frac{\partial V}{\partial T}\right)_P} - P$$

Systems With More Than Two Independent Variables

The greatest advantage in the use of Jacobians in thermodynamics is the derivation of relations where systems require more than two independent variables. The transition mathematically, thanks to Crawford, requires very little additional know-how beyond that needed for the manipulation of determinants of order greater than two. The Crawford paper (6b) is highly recommended for the detailed treatment of the general n -variables case; some elements of this case will be given here.

In setting up a problem for a system which requires more than two independent variables, for example the temperature change accompanying the sudden or adiabatic stretching of a metal bar, the fundamental equation for dE should be considered in the beginning. Thus in this particular system, if the metal is isotropic we have

$$dE = TdS - PdV + \tau dL \quad (7)$$

where τ = tension and dL = increment in length. Equation (7) would replace equation (1).

The dozen Maxwell relations between the six primary variables would begin to present a serious problem in bookkeeping whereas in terms of Jacobian notation there are only three Maxwell equations to keep track of. By means of Jacobians it is not too difficult for the student to venture into even more complex systems.

In general for a system that requires n independent variables for its description, dE may be written in the form of so-called conjugate forces, ϕ_i , and displacements, λ_i :

$$dE = TdS + \sum_{i=2}^n \phi_i d\lambda_i \quad (8)$$

Experiment or theory establishes the relation between a force and its conjugate displacement. The thermodynamic requirement for the validity of (7) or (8) is the absence of hysteresis effects, i.e., that λ_i be a unique function of ϕ_i . Equation (8) leads to corresponding equations for the remaining secondary variables, $H, A,$ and G .

$$H = E - \sum_{i=2}^n \phi_i \lambda_i; \quad dH = TdS - \sum_{i=2}^n \lambda_i d\phi_i \quad (9)$$

$$A = E - TS; \quad dA = -SdT + \sum_{i=2}^n \phi_i d\lambda_i \quad (10)$$

$$G = E - TS - \sum_{i=2}^n \phi_i \lambda_i; \quad dG = -SdT - \sum_{i=2}^n \lambda_i d\phi_i \quad (11)$$

Two matters have to be considered at this point: one is the manipulation of higher order functional determinants; the other is the establishment of the many Maxwell relations in Jacobian form. The manipulation of higher order determinants for thermodynamics centers about the rule of signs and follows the rule that the sign of the Jacobian is *changed* when a *neighboring* pair of variables either in the numerator or denominator is interchanged. Cancellation of a common variable in the numerator and denominator follows the same procedure as that used previously; i.e., a cancelled variable causes a reduction of the order of the Jacobian and the cancelled variable appears outside the partial. For example, for the Jacobian

$$J_1 = \frac{\partial(\phi_1, \phi_2, \lambda_3)}{\partial(\lambda_1, \lambda_2, \lambda_3)} = \begin{vmatrix} \left(\frac{\partial\phi_1}{\partial\lambda_1}\right)_{\lambda_2\lambda_3} & \left(\frac{\partial\phi_2}{\partial\lambda_1}\right)_{\lambda_2\lambda_3} \\ \left(\frac{\partial\phi_1}{\partial\lambda_2}\right)_{\lambda_1\lambda_3} & \left(\frac{\partial\phi_2}{\partial\lambda_2}\right)_{\lambda_1\lambda_3} \end{vmatrix}$$

whereas

$$J_2 = \frac{\partial(\phi_1 \lambda_3 \phi_2)}{\partial(\lambda_1 \lambda_2 \lambda_3)} = -J_1$$

In all this it is being assumed that a given partial derivative, $(\partial z / \partial y_1)_{y_2 \dots y_n}$, may be written as the Jacobian

$$\frac{\partial(z, y_2, \dots, y_n)}{\partial(y_1, y_2, \dots, y_n)}$$

As for the Maxwell equations, Crawford (6b) has shown that for a system of n independent variables where we write equation (8) in general form

$$dE = \phi_1 d\lambda_1 + \phi_2 d\lambda_2 + \phi_3 d\lambda_3 + \dots \quad (12)$$

it follows that

$$J(\phi_1, \lambda_1)_{x_2 \dots x_n} + J(\phi_2, \lambda_2)_{x_3 \dots x_n} + J(\phi_3, \lambda_3)_{x_4 \dots x_n} + \dots = 0 \quad (13)$$

Here the conjugate pair, (T, S) has been considered as one of the members of equation (13) and the x_s are the selected independent variables of the $2n$ primary set of variables. The important point for present purposes is that if the independent variables are chosen so that there is one from each conjugate set, then equation (13) yields $n(n-1)/2$ Maxwell equations, these being, of course, in Jacobian form. This may be summarized in general terms

$$\frac{\partial(\phi_j, \lambda_j)}{\partial(x_j, x_k)_{x_i \dots}} + \frac{\partial(\phi_k, \lambda_k)}{\partial(x_j, x_k)_{x_i \dots}} = 0 \quad (14)$$

where $j = 1, 2, \dots, n$; $j \neq k$; i takes on all values except j and k , and $(x_1 \dots x_n)$ are non-conjugate primary variables.

To illustrate the applicability of the above we will consider a few simple examples involving third order determinants. Returning to the case of the adiabatic extension of a metal bar under constant pressure, we consider finding a relationship for $(\partial T / \partial \tau)_{SP}$, selecting

as our set of independent variables T, P , and τ , i.e., members of the ϕ or "force" set. As may be seen from equation (7) we write

Step 1.

$$\left(\frac{\partial T}{\partial \tau}\right)_{SP} = \frac{\partial(T, S, P)}{\partial(\tau, S, P)} = \frac{\partial(T, S, P)}{\partial(T, P, \tau)} = -\frac{\left(\frac{\partial S}{\partial \tau}\right)_{T, P}}{\left(\frac{\partial S}{\partial T}\right)_{P, \tau}}$$

Step 2. No secondary variables to be removed.

Step 3. Required Maxwell equation:

$$\frac{\partial(T, S)}{\partial(T, \tau)_P} + \frac{\partial(\tau, L)}{\partial(T, \tau)_P} = 0$$

or

$$\left(\frac{\partial S}{\partial \tau}\right)_{TP} = \left(\frac{\partial L}{\partial T}\right)_{\tau P}$$

Also

$$C_{P\tau} = T \left(\frac{\partial S}{\partial T}\right)_{P\tau}$$

Substitution in Step 1 yields

$$\left(\frac{\partial T}{\partial \tau}\right)_{SP} = -\frac{T \left(\frac{\partial L}{\partial T}\right)_{\tau P}}{C_{P\tau}}$$

Since metals possess positive values for $(\partial L / \partial T)_{\tau P}$ we expect a cooling effect in stretching the bar. The opposite effect would be expected for rubber where $(\partial L / \partial T)_{\tau P}$ is known to be negative.

Finally we consider the problem of obtaining an expression for the difference in heat capacity $(C_{P\mathcal{H}} - C_{P\mathcal{G}})$, for an isotropic substance in a magnetic field, \mathcal{H} , where \mathcal{G} is the intensity of magnetization. The equation for dE may be written as

$$dE = TdS - PdV + \mathcal{H}d\mathcal{G}$$

Clearly an expression for both $C_{P\mathcal{H}}$ and $C_{P\mathcal{G}}$ in terms of the same set of independent variables is called for. Suppose one selects a mixed set, T, P , and \mathcal{G} , then taking $C_{P\mathcal{H}}$ which is equivalent to

$$C_{P\mathcal{H}} = T \left(\frac{\partial S}{\partial T}\right)_{P\mathcal{H}}$$

we write

$$T \left(\frac{\partial S}{\partial T}\right)_{P\mathcal{H}} = T \frac{\partial(S, P, \mathcal{H})}{\partial(T, P, \mathcal{H})} = T \frac{\partial(S, P, \mathcal{H})}{\partial(T, P, \mathcal{G})} \frac{\partial(T, P, \mathcal{G})}{\partial(T, P, \mathcal{H})}$$

or

$$C_{P\mathcal{H}} = T \left\{ \left(\frac{\partial S}{\partial T}\right)_{P\mathcal{G}} \left(\frac{\partial \mathcal{H}}{\partial \mathcal{G}}\right)_{PT} - \left(\frac{\partial S}{\partial \mathcal{G}}\right)_{PT} \left(\frac{\partial \mathcal{H}}{\partial T}\right)_{P\mathcal{G}} \right\} / \left(\frac{\partial \mathcal{H}}{\partial \mathcal{G}}\right)_{PT}$$

Noting that the appropriate Maxwell equation is

$$\frac{\partial(T, S)}{\partial(T, \mathcal{G})_P} + \frac{\partial(\mathcal{H}, \mathcal{G})}{\partial(T, \mathcal{G})_P} = 0$$

or

$$\left(\frac{\partial S}{\partial \mathcal{G}}\right)_{PT} = -\left(\frac{\partial \mathcal{H}}{\partial T}\right)_{P\mathcal{G}}$$

and that

$$T \left(\frac{\partial S}{\partial T}\right)_{P\mathcal{G}} = C_{P\mathcal{G}}$$

one can readily obtain the expression

$$C_{PH} - C_{P\beta} = T \left(\frac{\partial \mathcal{C}}{\partial T} \right)_{P\beta}^2 / \left(\frac{\partial \mathcal{C}}{\partial \beta} \right)_{TP}$$

While these examples may still be managed without the use of Jacobians it should not be difficult to realize their great usefulness if terms had been involved which considered the system anisotropic and/or where the so-called work terms were combined (e.g., $\tau dL + \mathcal{F}cd\mathcal{G}$, etc.). These more complex systems involving many Maxwell relations or so-called cross effects are systems that have been of continued interest in the study of the properties of substances, particularly in the solid state.

Literature Cited

- (1) HAKALA, R. W., *J. CHEM. EDUC.* **41**, 99 (1964).
- (2) SHAW, *Phil. Trans. Roy. Soc. London A* **234**, 299 (1935).
- (3) BREEN, D. E., *J. CHEM. EDUC.* **41**, 289 (1964).
- (4) CARROLL, B., AND LEHRMAN, A., *J. CHEM. EDUC.* **24**, 389 (1947).
- (5) LANDAU, L. D., AND LIFSHITZ, E. M., "Statistical Physics," Addison Wesley, Reading, Mass., 1958.
- (6) CRAWFORD, F. H. (a) *Am. J. Phys.* **17**, 1 (1949); (b) *Proc. Am. Acad. Arts Sci.* **78**, 165 (1950); (c) *Proc. Am. Acad. Arts Sci.* **83**, 191 (1955). (d) Also see "Heat, Thermodynamics and Statistical Physics," Harcourt Brace & World Inc., New York, 1963.
- (7) MORGNEAU, H., AND MURPHY, G. M., "The Mathematics of Physics and Chemistry," 2nd ed., D. van Nostrand Co. Inc., New York, 1956.

