PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

The Derivation of Thermodynamical Relations for a Simple System

A. Norman Shaw

Phil. Trans. R. Soc. Lond. A 1935 **234**, 299-328
doi: 10.1098/rsta.1935.0009

X. The Derivation of Thermodynamical Relations for a Simple System

By A. NORMAN SHAW, *F.R.S.C., Professor of Physics, McGill University, Montreal*

(Communicated by A. S. EVE, F.R.S.—Received July 7, 1934—Read January 24, 1935)

CONTENTS

1—*Introduction*

In the majority of articles and texts requiring or explaining the applications of thermodynamics, numerous relations between partial derivatives are obtained or discussed without the adoption of a systematic method. No uniform procedure has been followed heretofore for finding quickly and easily the relation between any given derivative, and any permissible set of other derivatives chosen for reference. There is a very common practice of dealing with useful relations by the method of "presentation followed by verification," which is most unsatisfactory. A few tables are available; in particular, the "Condensed Collection of Thermodynamical Formulas," by P. W. BRIDGMAN (Harvard Univ. Press) is useful and covers a large range; but in all current procedures the task of expressing a first or second partial derivative in terms of a set of others, remains in general most laborious. In the cases when the various derivatives of a chosen reference set had different pairs of independent variables, many transformations of possible interest have been neglected as altogether too complicated or too tedious for solution.

If we desire to evaluate some partial derivative which cannot be obtained directly from experimental data, we should naturally choose other derivatives which have been found with the desired precision, and use them to calculate the former. Curiously, it appears that little advantage is taken of this possible procedure; often we find that the better-known standard relations are used, when the included derivatives may not have been determined with as high a precision as some others.

With the aid of a simple Jacobian notation, it is the object of this paper to outline a systematic direct procedure capable of effecting any desired transformations and yielding many millions of relations with a minimum of analysis. This may be facilitated by two or three tables, which, while much more compact than previously existing ones, contain data for a great many more transformations. The derivation of these tables will be found straightforward, and the art of using them easily, may be acquired rapidly.

Throughout this article our attention will be confined to the case of a simple system, under circumstances where three related thermodynamical variables are sufficient to describe its state. The extension to cases involving change of mass may be developed along similar lines later.

It was considered essential to present this type of work in a sufficiently elementary manner and with adequate instructions, so that it might be of immediate use to teachers and students of thermodynamics as well as to those who will apply it in physics, chemistry, and engineering.

Part I—A Systematic Procedure for the Transformation of Partial First Derivatives and the Rapid Determination of Relations between them

2—*Tables of Values for* J (x, y)

If the use of an ordinary slide-rule and its great value are understood, the theory of its construction and application will receive closer attention and interest; similarly, it is appropriate here to show first the simplicity of the use, and the remarkable scope of Table I, proceeding later in our discussion to review the elements of the underlying theory.

In Table I, J (x, y) represents

$$\left(\frac{\partial x}{\partial \alpha}\right)_\beta \cdot \left(\frac{\partial y}{\partial \beta}\right)_\alpha - \left(\frac{\partial x}{\partial \beta}\right)_\alpha \cdot \left(\frac{\partial y}{\partial \alpha}\right)_\beta$$

where either x or y may be any one of p, v, T, S, E, I, F, or G, which are defined in the list of symbols at the end of this paper (Section 19). The independent variables α and β are unspecified in the table, and may be chosen arbitrarily from these or other quantities, provided it is true in every case, that x and y are each functions (either known or unknown) of α and β.

The important fundamental relation, $b^2 + ac - ln = 0$ mentioned at the top of Table I, is derived in Section 13, and may be assumed for the time being.

TABLE I—TABLE OF VALUES OF J (x, y)

$b^2 + ac - ln = 0$

$y\rightarrow$ $x\downarrow$	p	v	T	S	E	I	F	G	Q	W
p	0	b	l	c	$\mathrm{T}c - pb$	$\mathrm{T}c$	$-\mathrm{S}l - pb$	$-\mathrm{S}l$	$\mathrm{T}c$	pb
v	$-b$	0	a	n	$\mathrm{T}n$	$\mathrm{T}n - vb$	$-\mathrm{S}a$	$-\mathrm{S}a - vb$	$\mathrm{T}n$	0
T	$-l$	$-a$	0	b	$\mathrm{T}b + pa$	$\mathrm{T}b - vl$	pa	$-vl$	$\mathrm{T}b$	$-pa$
S	$-c$	$-n$	$-b$	0	pn	$-vc$	$\mathrm{S}b + pn$	$\mathrm{S}b - vc$	0	$-pn$
E	$-\mathrm{T}c + pb$	$-\mathrm{T}n$	$-\mathrm{T}b - pa$	$-pn$	0	$-\mathrm{T}vc$ $- p(\mathrm{T}n - vb)$	$\mathrm{T}(\mathrm{S}b + pn)$ $+ p\mathrm{S}a$	$\mathrm{T}(\mathrm{S}b - vc)$ $+ p(\mathrm{S}a + vb)$	$-p\mathrm{T}n$	$-\mathrm{T}pn$
I	$-\mathrm{T}c$	$-\mathrm{T}n + vb$	$-\mathrm{T}b + vl$	vc	$\mathrm{T}vc$ $+ p(\mathrm{T}n - vb)$	0	$\mathrm{T}(\mathrm{S}b + pn)$ $- v(\mathrm{S}l + pb)$	$\mathrm{T}(\mathrm{S}b - vc)$ $- v\mathrm{S}l$	$v\mathrm{T}c$	$-\mathrm{T}pn + vpb$
F	$\mathrm{S}l + pb$	$\mathrm{S}a$	$-pa$	$-\mathrm{S}b - pn$	$-\mathrm{T}(\mathrm{S}b + pn)$ $- p\mathrm{S}a$	$-\mathrm{T}(\mathrm{S}p + pn)$ $+ v(\mathrm{S}l + pb)$	0	$\mathrm{S}vl$ $+ p(\mathrm{S}a + vb)$	$-\mathrm{ST}b - p\mathrm{T}n$	$\mathrm{S}pa$
G	$\mathrm{S}l$	$\mathrm{S}a + vb$	vl	$-\mathrm{S}b + vc$	$-\mathrm{T}(\mathrm{S}b - vc)$ $- p(\mathrm{S}a + vb)$	$-\mathrm{T}(\mathrm{S}b - vc)$ $+ v\mathrm{S}l$	$-\mathrm{S}vl$ $- p(\mathrm{S}a + vb)$	0	$-\mathrm{ST}b + v\mathrm{T}c$	$\mathrm{S}pa + vpb$
Q	$-\mathrm{T}c$	$-\mathrm{T}n$	$-\mathrm{T}b$	0	$p\mathrm{T}n$	$-v\mathrm{T}c$	$\mathrm{ST}b + p\mathrm{T}n$	$\mathrm{ST}b - v\mathrm{T}c$	0	$-\mathrm{T}pn$
W	$-pb$	0	pa	pn	$\mathrm{T}pn$	$\mathrm{T}pn - vpb$	$-\mathrm{S}pa$	$-\mathrm{S}pa - vpb$	$\mathrm{T}p\ n$	0

3—*The Interpretation of Table I*

The value of J (x, y), in terms of one or more of a, b, c, l, n, p, v, T and S, for any x, given in the left-hand column, and any y, given in the top row, is found at the intersection of the specified row and column; for example:—

$$J(v, E) = Tn\ ;\ J(S, F) = Sb + pn\ ;\ \text{etc.}$$

Conversely, the values of a, b, c, l and n, chosen as five "reference Jacobians," may be read at once, for example:—

$$b = J(p, v) = J(T, S)\ ;\ n = J(v, S) = J(v, E)/T = J(S, E)/p\ ;\ \text{etc.}$$

The value of any first partial derivative is obtained by inspection from the ratio of two Jacobians, since, as shown in Section 11, we have

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{J(x, z)}{J(y, z)}.$$

For example:

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{b}{l}\ ;\ \left(\frac{\partial S}{\partial p}\right)_T = -\frac{b}{l}\ ;\ \left(\frac{\partial F}{\partial E}\right)_I = \frac{-T(Sb + pn) + v(Sl + pb)}{-Tvc - p(Tn - vb)}\ ;$$

$$\left(\frac{\partial F}{\partial T}\right)_v = -S\ ;\ \left(\frac{\partial Q}{\partial T}\right)_v = \frac{Tn}{a} = \frac{T(b^2 + ac)}{al}\ ;\ \text{etc.}$$

It will be seen that any partial first derivative may be expressed in this manner in terms of not more than three ratios of "reference Jacobians," that is, three other partial derivatives, which are independent. By successive applications it may be shown that any partial first derivative may be expressed in terms of any specified three others which are independent; in these transformations, any of p, v, T and S may, in general, also be included.

4—*The Construction of Table I*

It is a simple and short procedure to reconstruct Table I from memory. It is only necessary to recall:—(1) the meanings of the symbols, p, v, T, S, E, I, F, G, Q and W, or any other appropriate set; and, (2) the meanings of, and relation between, a, b, c, l and n (or any other permissible choice of five reference Jacobians), which can be done mnemonically merely by remembering expression 46A, Section 13.

The upper left-hand part of the table for p, v, T and S may then be filled in by inspection. The definitions of E, I, F and G give at once the well-known expressions for dE, dI, dF and dG, which are visualized in terms of Jacobians; for example, the familiar $dE = TdS - pdv$ is visualized as $J(E, x) = TJ(S, x) - pJ(v, x)$ where x is any permissible variable, and thus, $J(E, p) = TJ(S, p) - pJ(v, p) = -Tc + pb$. Similarly, all the lower left-hand part may be filled in without auxiliary analysis. For the Q and W rows, use is made of $J(Q, x) = TJ(S, x)$ and $J(W, x) = pJ(v, x)$, always recalling that in the case of these two symbols it is only the Jacobians which are functions of α and β—there are no functions Q and W. (This limitation, excludes their use from any calculation which would require that dQ, and dW are complete differentials, for example, in $J[J(x, \alpha), \beta] = J[J(x, \beta), \alpha]$ it is not permissible to use Q or W for x, because $\partial^2 x/\partial\alpha \,.\, \partial\beta = \partial^2 x/\partial\beta \,.\, \partial\alpha$ is not true in general unless dx is a complete differential.)

The right-hand upper part of the table follows from the lower left, simply by changing signs, thus $J(p, E) = -J(E, p) = Tc - pb$, etc.

The lower right-hand part which is only occasionally required, is obtained by resolving the Jacobians as before, and using the parts of the table already completed. For example,

$$J(E, G) = TJ(S, G) - pJ(v, G) = T(Sb - vc) + p(Sa + vb) \,.$$

The whole chart can be recaptured in this way in only a few minutes, but for an ordinary single problem the parts of the table required may, if no table is available, be recalled in less than a minute, sometimes in a few seconds. For example, if expression 46A (Section 13) is borne clearly in mind, such simple transformations as the following can be solved mentally with the aid of perhaps one line of writing, but without reference to the table :—

Transform $C_v = (\partial Q/\partial T)_v$ *into groups of derivatives in which any two of* p, v, T *and* S *are in turn chosen as independent variables.*

Since $b^2 + ac - ln = 0$, we have, by inspection,

$$C_v = Tn/a = T(b^2 + ac)/al = Tnc/(nl - b^2)$$

in which α and β may represent any permissible pair of variables. The various resultant expressions may be read from the above equivalents for C_v without further writing ; for example, if we take the case $p = \alpha$ and $S = \beta$, we read from $C_v = Tnc/(nl - b^2)$, as follows :—

$$C_v = T\left(\frac{\partial v}{\partial p}\right)_S \Big/ \left[\left(\frac{\partial v}{\partial p}\right)_S \cdot \left(\frac{\partial T}{\partial S}\right)_p - \left(\frac{\partial v}{\partial S}\right)_p^2\right].$$

and we would obtain, similarly, the expressions for other values of α and β.

It will be noted in the above case, how it was possible to avoid the appearance of $\partial(v, T)/\partial(p, S)$ which cannot be expressed by a single partial derivative.

However, by the use of the table the final result could have been obtained with less effort. If derivatives involving E, I, F, and G are considered, as illustrated in examples given in other sections, it is obvious that the table is essential, if speed in proceeding directly to the solution is desired.

5—*Three Examples Illustrating the Use of Table I in Simple Cases*

The following examples are chosen to illustrate the value of these methods in making it possible to proceed in a systematic way to connect any partial first derivative, with three others which are independent, provided each variable which appears is a function (known or unknown) of two variables, α and β. For the sake of comparison with the ordinary lengthy methods, the first ones chosen are well-known elementary relations.

1—*Find the relation between* κ_T, α_p, C_p *and* C_v *for any simple substance.*

$$\left[\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T, \alpha_p = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p, C_p = \left(\frac{\partial Q}{\partial T}\right)_p, C_v = \left(\frac{\partial Q}{\partial T}\right)_v\right]$$

The solution in two lines:—

$$a = -v\kappa_T l,\ b = v\alpha_p l,\ c = (C_p/T)l,\ n = (C_v/T)\ a = -(vC_v\kappa_T/T)\ l$$

hence

$$v^2\alpha_p{}^2 - \left(\frac{vC_p\kappa_T}{T}\right) + \left(\frac{vC_v\kappa_T}{T}\right) = 0 \quad or \quad C_p - C_v = Tv\alpha_p{}^2/\kappa_T$$

(*Note*—The preliminary part, done mentally, term by term with the aid of Table I, should be obvious—for example

$$\kappa_T = -\frac{1}{v}\cdot\left(\frac{J\ (v, T)}{J\ (p, T)}\right) = -\frac{a}{vl}\ \therefore a = -v\kappa_T l$$

as noted, and similarly for the other terms. In the second line these are substituted in the fundamental equation $b^2 + ac - ln = 0$, which must give the desired relation. It will be observed why the l cancels out, and that the same result would follow, by putting any one of a, b, c, l and n equal to unity at the start.)

2—*Find the relation between*

$$\left(\frac{\partial E}{\partial p}\right)_T, \left(\frac{\partial T}{\partial p}\right)_I, C_p \text{ and } \left(\frac{\partial\ (pv)}{\partial p}\right)_T$$

for a simple substance.

Solution—From Table I, we read,

$$\left(\frac{\partial E}{\partial p}\right)_T = \frac{-Tb - pa}{l}, \quad \left(\frac{\partial T}{\partial p}\right)_I = \frac{Tb - vl}{Tc}$$

$$C_p = \frac{Tc}{l}, \qquad \left(\frac{\partial\ (pv)}{\partial p}\right)_T = \frac{pa}{l} + v.$$

This is a good example of many cases where the relation can be seen, by inspection, at this stage. It is apparent that the sum of the first and fourth is equal to minus the product of the other two, that is,

$$-C_p\left(\frac{\partial T}{\partial p}\right)_I = \left(\frac{\partial E}{\partial p}\right)_T + \left(\frac{\partial\ (pv)}{\partial p}\right)_T.$$

If this escapes attention, one proceeds as in example (1). It may be observed that if one of a, b, c, l and n does not appear, there will always be two relations which may be equated, and then it is not necessary to evaluate the missing Jacobian with the aid of $b^2 + ac - ln = 0$. In this case we may therefore proceed alternatively as follows :—

$$\frac{c}{l} = \frac{C_p}{T}, \quad \frac{b}{l} = \frac{C_p}{T}\left(\frac{\partial T}{\partial p}\right)_I + \frac{v}{T}, \quad \text{and}$$

$$\frac{a}{l} = -\frac{C_p}{p}\left(\frac{\partial T}{\partial p}\right)_I - \frac{v}{p} - \frac{1}{p}\left(\frac{\partial E}{\partial p}\right)_T = \frac{1}{p}\left(\frac{\partial (pv)}{\partial p}\right)_T - \frac{v}{p},$$

and it will be seen at once that the desired relation (given above) follows from the equation for the two values of a/l. This solution requires only three or four lines of actual writing.

3—*Connect* $(\partial E/\partial S)_F$ *with* C_v *and, if possible, only one other partial derivative.*

From Table I, $C_v = Tn/a$, and

$$\left(\frac{\partial E}{\partial S}\right)_F = \frac{T\,(Sb + pn) + pSa}{Sb + pn} = T + \frac{pSa}{Sb + pn}$$

$$= T + \frac{p\,S}{S\,\dfrac{b}{a} + \dfrac{p}{T}\,C_v}.$$

Substitution for b/a, of either $-(\partial p/\partial T)_v$ or $-(\partial S/\partial v)_T$ in the above expression solves the problem. Another solution containing only two derivatives can similarly be obtained in terms of C_v and either $-(\partial p/\partial S)_v$ or its equivalent, $(\partial T/\partial v)_S$.

6—*The Choice of "Reference Derivatives" when the Independent Variables are to be the Same Throughout*

In the use of Table I, the ratios a/c and l/n (and their reciprocals) do not reduce to single partial derivatives, since $a/c = \partial\,(v, T)/\partial\,(p, S)$ and $l/n = \partial\,(p, T)/\partial\,(v, S)$. These ratios may be avoided easily by the use of the relation $b^2 + ac - ln = 0$, or its equivalent if other Jacobians are chosen as the basis of reference.

It will be seen that :—

(1) If $\alpha = v$ and $\beta = T$, that is $a = 1$, we must use $nl - b^2$ for c to avoid c/a.

(2) If $\alpha = p$ and $\beta = S$, that is $c = 1$, we must use $nl - b^2$ for a to avoid a/c.

(3) If $\alpha = p$ and $\beta = T$, that is $l = 1$, we must use $b^2 + ac$ for n to avoid n/l.

(4) If $\alpha = v$ and $\beta = S$, that is $n = 1$, we must use $b^2 + ac$ for l to avoid l/n.

(5) If $\alpha = p$ and $\beta = v$, that is $b = 1$,
(6) If $\alpha = T$ and $\beta = S$, that is $b = 1$,
} Single partial derivatives survive in all ratios, if $b = 1$.

The following tabulated data may be obtained readily by inspection of Table I, but it serves to call attention to the results and the relative values of the choices of independent variables, when one is seeking expressions (containing the same α and β throughout) which will involve the minimum number of derivatives for which good measurements are available. In practice some derivatives have been measured more accurately than others, and it becomes possible to make the best use of these, rapidly.

All permissible derivatives at constant r (given below), viz., all of type $(\partial x/\partial y)_r$, are expressed by Table I in terms of the Jacobians below :		In avoiding the occurrence of ratios of the type J (x, y)/J (z, w), $(\partial x/\partial y)_r$ must be expressed in terms of the groups below :				
		If $a = 1$	If $b = 1$	If $c = 1$	If $l = 1$	If $n = 1$
When $r = p$	b, c, l	b, l, n	c, l	b, l	b, c	a, b, c
,, $r = v$	a, b, n	b, n	a, n	b, l, n	a, b, c	a, b
,, $r = \mathrm{T}$	a, b, l	b, l	a, l	b, l, n	a, b	a, b, c
,, $r = \mathrm{S}$	b, c, n	b, l, n	c, n	b, n	a, b, c	b, c
,, $r = \mathrm{E}$	a, b, c, n	b, l, n	a, c, n	b, l, n	a, b, c	a, b, c
,, $r = \mathrm{I}$	b, c, l, n	b, l, n	c, l, n	b, l, n	a, b, c	a, b, c
,, $r = \mathrm{F}$	a, b, l, n	b, l, n	a, l, n	b, l, n	a, b, c	a, b, c
,, $r = \mathrm{G}$	a, b, c, l	b, l, n	a, c, l	b, l, n	a, b, c	a, b, c

We see, for example, if we are considering any permissible $(\partial x/\partial y)_{\mathrm{S}}$ whatever, that it may be expressed at once in terms of b and n, if $c = 1$, that is, in terms of either $(\partial v/\partial \mathrm{S})_p$, and $(\partial v/\partial p)_{\mathrm{S}}$, or $(\partial \mathrm{T}/\partial p)_{\mathrm{S}}$ and $(\partial v/\partial p)_{\mathrm{S}}$. Thus, as an illustration, we have from Table I,

$$\left(\frac{\partial \mathrm{G}}{\partial \mathrm{E}}\right)_{\mathrm{S}} = \frac{-\mathrm{S}b + vc}{-pn} = \frac{-\mathrm{S}\left(\dfrac{\partial v}{\partial \mathrm{S}}\right)_p + v}{-p\left(\dfrac{\partial v}{\partial p}\right)_{\mathrm{S}}}$$

and if we require the independent variables to be, let us say, p and T, then $l = 1$; and a, b, and c will appear, as follows :—

$$\left(\frac{\partial \mathrm{G}}{\partial \mathrm{E}}\right)_{\mathrm{S}} = \frac{-\mathrm{S}b + vc}{-pn} = \frac{-\mathrm{S}b + vc}{-p\,(b^2 + ac)} = \frac{-\mathrm{S}\left(\dfrac{\partial v}{\partial \mathrm{T}}\right)_p + v\left(\dfrac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_p}{-p\left[\left(\dfrac{\partial v}{\partial \mathrm{T}}\right)_p^2 + \left(\dfrac{\partial v}{\partial p}\right)_{\mathrm{T}} \cdot \left(\dfrac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_p\right]}.$$

In the same way we may get equally rapidly, the transformations for $a = 1$, $b = 1$, and $n = 1$.

Similarly, any derivative, common or uncommon, may be transformed rapidly from expression in terms of one set to that in terms of another ; and it is possible to see in advance which derivatives will be included and which cases will be degenerate.

The same possibility of comparing the number and choice of derivatives in advance, may be extended in the same manner to cases when α and β are chosen from variables other than p, v, T and S.

After only a short experience of the use of Table I, the user will find that reference to it is quite adequate to reveal the points explained in this section when they are required. The tabulated data, above, become self-evident, and have only been necessary here as a means of explaining an important aspect of these methods.

7—*To Express any Given First Partial Derivative in Terms of Three Chosen "Reference Derivatives" in which the Independent Variables may be Different Pairs*

In this particular case we have to deal with problems for which the old customary methods usually lead to extremely tedious and lengthy analysis, and no tables are available. Often, the derivatives which can be numerically evaluated most accurately do not have the same independent variables, and if we wish to obtain the value of another derivative which cannot be determined experimentally, it is desirable to be able to express it quickly in terms of any chosen set, for which accurate observations are available.

The procedure is not quite so rapid as when the pairs of independent variables in the "reference derivatives" are the same, but the additional auxiliary analysis is in each case elementary and straightforward. The three reference derivatives are first expressed in terms of a, b, c, l and n, by means of Table I, or otherwise. Then, using these expressions as three simultaneous equations, the values of three of a, b, c, l and n are calculated in terms of the given three reference derivatives and a fourth member of a, b, c, l and n. This fourth member will later disappear in all ratios, or in cases where it is unity; the remaining fifth member, if it appears, may always be evaluated with the aid of $b^2 + ac - ln = 0$. These values of a, b, c, l, n in terms of the chosen derivatives may now be substituted in the expression for the original derivative as given by Table I, and only the three chosen derivatives will remain. The simplicity of this procedure may be illustrated most easily by an example involving one of the more complicated expressions.

Given the specific heat at constant pressure (C_p), *the cooling effect at constant internal energy* (μ_E), *and the adiabatic cooling effect* (μ_S), *find the variation of internal energy with temperature at constant* G.

We have to express $(\partial E/\partial T)_G$ in terms of C_p, μ_E and μ_S. From Table I, we have

$$\left(\frac{\partial E}{\partial T}\right)_G = \frac{-T(Sb - vc) - p(Sa + vb)}{vl}.$$

Also we have

$$\left.\begin{aligned} C_p &= Tc/l \\ \mu_E &= (\partial T/\partial p)_E = (Tb + pa)/(Tc - pb) \\ \mu_S &= (\partial T/\partial p)_S = b/c \end{aligned}\right\} \text{therefore} \left\{\begin{aligned} c &= l\,C_p/T \\ b &= l\,C_p\mu_S/T \\ a &= l\,C_p\,(\mu_E - \mu_S - p\mu_E\mu_S/T)/p. \end{aligned}\right.$$

Substituting in the expression for $(\partial E/\partial T)_G$ we get at once on simplification,

$$\left(\frac{\partial E}{\partial T}\right)_G = C_p\left(1 - \frac{p}{T}\mu_S\right)\left(1 - \frac{S}{v}\mu_E\right).$$

The same result follows, of course, if we had temporarily retained some Jacobian other than l, or chosen a different set of three and used $b^2 + ac - ln = 0$ if required. The one hundred and thirty-five general expressions on pp. 523–526 of H. L. CALLENDAR's "Properties of Steam" (ARNOLD, 1920), may each, for example, be derived rapidly in this way, and alternative forms added in great numbers. Some of the equations in the list just quoted are not reduced to the minimum number of derivatives, and the form of corresponding expressions is not always retained in a systematic way; by the present methods any such desired relation may be obtained rapidly and systematically. Furthermore, by combination with the necessary additional relations, all the reduced values for the case of dry steam (or any other special case which is covered by specific additional relations) may be obtained by the construction of simple auxiliary tables of the type IA, discussed in Section 8. (The expression for $(\partial E/\partial T)_G$, above, will be seen to be the same as that given by CALLENDAR (*loc. cit.*) when the necessary change in notation is made, and it is also noted that he retains a fourth derivative C_G which will be seen to be reducible to v/S.)

If, as another example, it had been desired, instead, to express $(\partial E/\partial T)_G$, (or any other derivative) in terms of the three "cooling effects," μ_v, μ_S, and μ_I, one would find, first, in the same way as before, that

$$a = \frac{-v\,\mu_v\,\mu_S}{T\,(\mu_S - \mu_I)}\,l,\quad b = \frac{v\,\mu_S}{T\,(\mu_S - \mu_I)}\,l,\ \text{and}\ c = \frac{v}{T\,(\mu_S - \mu_I)}\,l$$

and hence by substitution that

$$\left(\frac{\partial E}{\partial T}\right)_G = \frac{v\,T - (pv + TS)\,\mu_S + p\,S\,\mu_v\,\mu_S}{T\,(\mu_S - \mu_I)}$$

and similarly for any other desired transformation of this type. It may be observed, in passing, that this expression is equal to the specific heat at constant volume, in those cases when it is permissible to assume $pv = RT$; the detection of such secondary or special relations which are often of interest, is greatly facilitated by the use of tables for special cases, such as Table IA (Section 8).

8—*The Use of Table I when the Equation of State, or other Additional Conditions are given*

In a large number of cases a given equation of state is known to hold with sufficient accuracy over a specified range of conditions; also there are many cases in which some special relation may hold. In such circumstances, the expressions for the Jacobians may usually be reduced so that any ratio involves only one, and sometimes none of the partial derivatives of the given variables. If $f(p, v, T) = 0$, is known in full, it is possible to obtain the ratios between any two of X, Y, Z in $X dp + Y dv + Z dT = 0$, and hence any first derivative may be expressed in terms of not more than one (instead of three) chosen first derivatives, plus the usual variables.

In the case of a vapour kept saturated the first derivatives may be conveniently reduced to involve only $dp/d\mathrm{T}$ and C_v plus the usual variables.

In the case of radiation in an enclosure, with perfectly reflecting walls, all derivatives may be eliminated.

In Table IA a few such cases are summarized. While a reference to this auxiliary table greatly facilitates the resolution of a complicated expression involving several derivatives, it will be apparent that the values could be deduced easily as required.

The columns for $pv = \mathrm{RT}$, and for VAN DER WAAL's equation (and similarly for other equations of state) are deduced at once from the column under $f(p, v, \mathrm{T}) = 0$, the derivation of which is self-evident. In the case of a vapour kept saturated, the values are obtained by using $\mathrm{J}(p, \mathrm{T}) = 0$, and $\mathrm{J}(x, p) = \mathrm{J}(x, \mathrm{T}) \cdot (dp/d\mathrm{T})$, which are true if p is constant when T is constant. In the case of radiation, the values follow from the assumption that E/v is constant when T is constant, and the special relation $p = \mathrm{E}/3v$ for the pressure of electromagnetic radiation.

As an illustration of the convenience and the method of using this table, a few well-known relations are derived below. The brevity in derivation, and the value of a systematized procedure, become even more apparent in dealing with relatively elaborate expressions such as arise in making gas thermometer corrections, preparation of steam tables, etc.

In each case below the transformations are obtained at once from the tables—but may also be obtained, *ab initio*, following these methods, with almost the same speed.

i—*When* $pv = \mathrm{RT}$.

(*a*) *What is the adiabatic relation between p and v?*

$$\left(\frac{\partial p}{\partial v}\right)_{\mathrm{S}} = \frac{c}{n} = -\frac{\mathrm{C}_p}{\mathrm{C}_v} \cdot \frac{p}{v}\text{; hence } pv^{\gamma} = k, \text{ if } \gamma \text{ and S are constant.}$$

(*b*) *What is the value of* $\mathrm{C}_p - \mathrm{C}_v$?

$$\mathrm{C}_p - \mathrm{C}_v = \frac{\mathrm{T}c}{l} - \frac{\mathrm{T}n}{a} = -\frac{\mathrm{T}b^2}{la} = \frac{pv}{\mathrm{T}}.$$

(*c*) *What is the adiabatic relation between* T *and v?*

$$\left(\frac{\partial v}{\partial \mathrm{T}}\right)_{\mathrm{S}} = \frac{n}{b} = -\frac{\mathrm{C}_v}{p} = -\frac{\mathrm{C}_v}{\mathrm{T}(\mathrm{C}_p - \mathrm{C}_v)} = -\frac{v}{\mathrm{T}(\gamma - 1)}\text{; hence } v^{\gamma-1}\mathrm{T} = k, \text{ if}$$

S and γ are constant.

(*d*) *What is the "cooling effect" at constant total heat?*

$$\left(\frac{\partial \mathrm{T}}{\partial p}\right)_{\mathrm{I}} = \frac{\mathrm{T}b - vl}{\mathrm{T}c} = 0.$$

(*e*) *What is the true coefficient of expansion at constant pressure?*

$$\frac{1}{v}\left(\frac{\partial v}{\partial \mathrm{T}}\right)_p = \frac{b}{vl} = \frac{1}{\mathrm{T}}.$$

TABLE IA—VALUES OF a, b, c, l, AND n, IN SPECIAL CASES

	$J(x, y)$	Given $f(p, v, T) = 0$ and $X dp + Y dv + Z dT = 0$	If $pv = RT$ holds	If VAN DER WAAL's equation holds $\left(p + \frac{a'}{v^2}\right)(v - b') = RT$	For a vapour kept saturated $p = f(T)$	For Radiation in an enclosure with perfectly reflecting walls
a	$J(v, T)$	$\frac{X}{Z} b$	$-\frac{T}{p} b$	$-\frac{v - b'}{R} b$	$-\frac{dT}{dp} b$	$-\frac{T}{4p} b$
b	$J(p, v) = J(T, S)$	b	b	b	b	b
c	$J(p, S)$	$-\frac{Y}{Z}\frac{C_p}{T} b$	$\frac{C_p}{v} b$†	$\frac{1}{R}\left(p - \frac{a'}{v^2} + \frac{2a'b'}{v^3}\right)\frac{C_p}{T} b$	$\frac{dp}{dT} b$	$\frac{4p}{T} b$
l	$J(p, T)$	$-\frac{Y}{Z} b$	$\frac{T}{v} b$	$\frac{1}{R}\left(p - \frac{a'}{v^2} + \frac{2a'b'}{v^3}\right) b$	0	0
n	$J(v, S)$	$\left(\frac{X}{Z}\frac{C_p}{T} - \frac{Z}{Y}\right) b$*	$\left(\frac{v}{T} - \frac{C_p}{p}\right) b$*†	$\left(-\frac{(v-b')}{R}\frac{C_p}{T} + \frac{R}{\left(p - \frac{a'}{v^2} + \frac{2a'b'}{v^3}\right)}\right) b$	$-\frac{C_v}{T}\frac{dT}{dp} b$‡	$-\frac{3v}{T} b$‡

* n also equals $\frac{C_v}{T}\frac{X}{Z} b$, and this reduces to $-\frac{C_v}{p} b$ when $pv = RT$.

† In the case of a perfect gas, these reduce to $c = \frac{5}{2}\frac{p}{T} b$ and $n = -\frac{3}{2}\frac{v}{T} b$ when $C_v = \frac{3}{2} R$.

‡ C_p is infinite in this case.

(The determination of these results for the cases of other equations of state, proceeds in the same way, and illustrates the great saving in time when one passes to less familiar relations.)

ii—*Radiation in an enclosure.*

(*a*) *Given* $p = \frac{1}{3}E' = \frac{1}{3}(E/v) =$ *a function of* T *only, what is the relation between* E′ *and* T ?

$$\frac{dE'}{dT} = \frac{1}{v}\left(\frac{\partial E}{\partial T}\right)_v = \frac{Tn}{va} = \frac{12p}{T} = \frac{4E'}{T}; \text{ hence } E' = \sigma T^4. \quad (\text{Stefan's law.})$$

(*b*) *What is the adiabatic relation between* v *and* T ?

$$\left(\frac{\partial v}{\partial T}\right)_S = \frac{n}{b} = -\frac{3v}{T}; \text{ hence } vT^3 = k \text{ at constant S.}$$

(*c*) *Assuming* Wien's *displacement law* ($\lambda T = k_1$, *when* S *is constant*), *find a relation connecting the distribution of energy in the spectrum with* λ *and* T.

Using $E' = \dfrac{4S'}{3 \times 10^{10}} = \sigma T^4$, we have*

$$J(\lambda, S) = -\frac{k_1}{T^2} \,.\, J(T, S), \quad \text{and} \quad J(S', S) = k_2 T^3 J(T, S)$$

hence

$$e_\lambda = \left(\frac{\partial S'}{\partial \lambda}\right)_S = \frac{J(S', S)}{J(\lambda, S)} = k_3 T^5 = k_4 \lambda^{-5} = k_5 \lambda^{-5} f(\lambda \,.\, T),$$

where the various constants may be evaluated.

iii—*A liquid in equilibrium with its vapour.*

What is the connection between latent heat, the two specific volumes, and dp/dT ?

For unit mass, $L_T = \left(\dfrac{\partial Q}{\partial v}\right)_T (v_2 - v_1)$ by definition, and $\dfrac{dp}{dT} = \left(\dfrac{\partial p}{\partial T}\right)_v$ when p is a function of T only, hence

$$\frac{L_T}{v_2 - v_1} = \left(\frac{\partial Q}{\partial v}\right)_T = -\frac{Tb}{a} = T\frac{dp}{dT}.$$

(A simple derivation of Clapeyron's equation.)

9—*The Interpretation and Use of Table II*

Table II is merely an alternative, and is included here, because it constitutes a single compact chart which is adequate for the solution of a large fraction of the ordinary types of transformations, without need of reference to the larger tables, I and III.

* By inspection, we have $\lambda dT + Td\lambda = 0$ if S is constant, and therefore $\lambda J(T, S) = -TJ(\lambda, S)$; similarly, $J(E', x) = kJ(S', x) = \sigma J(T^4, x) = 4\sigma T^3 J(T, x)$ where x is any permissible variable.

TABLE II—CONDENSED TABLE OF VALUES FOR $J(x, y)$ when $\alpha = p$ and $\beta = T$ (FOR FIRST AND SECOND DERIVATIVES)

$x \downarrow$ $y \rightarrow$	p	v	T	S	x Any function of α and β
p	0	b	1	c	$J(p, x)$
v	$-b$	0	a	$b^2 + ac$	$aJ(p, x) + bJ(T, x)$
T	-1	$-a$	0	b	$J(T, x)$
S	$-c$	$-(b^2 + ac)$	$-b$	0	$-bJ(p, x) + cJ(T, x)$
E	$-Tc + pb$	$-T(b^2 + ac)$	$-Tb - pa$	$-p(b^2 + ac)$	$-(Tc - pb) J(x, T) + (Tb + pa) J(x, p)$
I	$-Tc$	$-T(b^2 + ac) + vb$	$-Tb + v$	vc	$-Tc J(x, T) - (v - Tb) J(x, p)$
F	$S + pb$	Sa	$-pa$	$-Sb - p(b^2 + ac)$	$(S + pb) J(x, T) + pa J(x, p)$
G	S	$Sa + vb$	v	$-Sb + vc$	$SJ(x, T) - vJ(x, p)$
Q	$-Tc$	$-T(b^2 + ac)$	$-Tb$	0	$-Tc J(x, T) + Tb J(x, p)$
W	$-pb$	0	pa	$p(b^2 + ac)$	$-pb J(x, T) - pa J(x, p)$
x	$J(x, p)$	$aJ(x, p) + bJ(x, T)$	$J(x, T)$	$-bJ(x, p) + cJ(x, T)$	0
y	$J(y, p)$	$aJ(y, p) + bJ(y, T)$	$J(y, T)$	$-bJ(y, p) + cJ(y, T)$	$J(y, p) J(x, T) - J(y, T) J(x, p)$
a	$-Y_2$	$bY_1 - aY_2$	Y_1	$cY_1 + bY_2$	$-Y_2 J(x, T) - Y_1 J(x, p)$
b	Y_3	$bY_2 + aY_3$	Y_2	$cY_2 - bY_3$	$Y_3 J(x, T) - Y_2 J(x, p)$
c	Y_4	$bY_3 + aY_4$	Y_3	$cY_3 - bY_4$	$Y_4 J(x, T) - Y_3 J(x, p)$
n	$2bY_3 + aY_4 - cY_2$	$bcY_1 + (2b^2 - ac)Y_2 + 3abY_3 + a^2Y_4$	$cY_1 + 2bY_2 + aY_3$	$c^2Y_1 + 3bcY_2 - (2b^2 - ac)Y_3 - abY_4$	$2bJ(b, x) + aJ(c, x) + cJ(a, x)$

$a = (\partial v/\partial p)_T$	$b = (\partial v/\partial T)_p = -(\partial S/\partial p)_T$	$c = (\partial S/\partial T)_p = C_p/T$	$n = b^2 + ac = \partial(v, S)/\partial(p, T) = aC_v/T$
$Y_1 = (\partial^2 v/\partial p^2)_T$	$Y_2 = -(\partial^2 S/\partial p^2)_T = \partial^2 v/\partial p \partial T$	$Y_3 = -(\partial^2 v/\partial T^2)_p = \partial^2 S/\partial p \partial T$	$Y_4 = -(\partial^2 S/\partial T^2)_p$

The upper part will be seen at a glance to be a condensation of Table I, and the lower part with the aid of equations, (36), (37) or (38), of Section 11, may be used to obtain any second partial derivative in terms of Y_1, Y_2, Y_3 and Y_4 when $l = 1$. If $\alpha = p$ and $\beta = T$ (that is, $l = 1$) the symbols in this table stand also for the derivatives given at the bottom.

Further explanations and illustrations of its use are omitted to avoid repetition; the application of the table will be quite apparent after a consideration of the sections dealing with Tables III and IV for which a more detailed discussion is required.

More additional analysis, in lieu of reference to Table I, is required if problems are of certain types, but, in general, Table II will be found useful as a compact summary of procedure for the rapid expression of any first or second partial derivative in terms of the reference set specified at the foot of this table.

Part II—Notes on the Theory and Use of Jacobians as Applied to First and Second Partial Derivatives

10—*Summary of Relations Useful in Manipulations of* J (x, y), *including Cases when* x *or* y *may be Functions of one or more Variables, each of which are Functions of* α *and* β

If x, y, or z represent functions of one or more of the variables given in the tables, it is, in general, necessary to express the Jacobian in full, differentiate and resolve in terms of the tabulated Jacobians. The following summary, provided for quick reference, makes this procedure both simple and rapid. The majority of the transformations are either obvious or easily deduced *ab initio*, but experience has shown that a ready list of them assists greatly in saving time and avoiding errors in analysis.

We have from our definitions :—

$$J(x, y) = \partial(x, y)/\partial(\alpha, \beta) = (\partial x/\partial\alpha)_\beta \cdot (\partial y/\partial\beta)_\alpha - (\partial y/\partial\alpha)_\beta \cdot (\partial x/\partial\beta)_\alpha \quad (1)$$

$$= A_x B_y - A_y B_x \text{ where } A_r = J(r, \beta), \text{ and } B_r = J(\alpha, r) \quad (2)$$

$$= J(x, \beta) \cdot J(\alpha, y) - J(y, \beta) \cdot J(\alpha, x)$$

$$= J(x, \alpha) \cdot J(y, \beta) - J(x, \beta) \cdot J(y, a) \quad (3)$$

$$= \{J(x, z) \cdot J(y, w) - J(x, w) \cdot J(y, z)\}/J(z, w) \quad (4)$$

where w is also a function of α and β.

It follows from these, that

$$J[f_1(x), f_2(y)] = A_{f_1} B_{f_2} - A_{f_2} B_{f_1} = f'_1(x) \cdot f'_2(y) \cdot J(x, y) \quad (5)$$

and

$$J[f_1(x, y), f_2(z, w)] = A_{f_1} B_{f_2} - A_{f_2} B_{f_1}$$
$$= X_1 Z_2 J(x, z) + X_1 W_2 J(x, w) + Y_1 Z_2 J(y, z) + Y_1 W_2 J(y, w) \quad (6)$$

where $X_1 = \left(\frac{\partial f_1}{\partial x}\right)_y$; $Y_1 = \left(\frac{\partial f_1}{\partial y}\right)_x$; $Z_2 = \left(\frac{\partial f_2}{\partial z}\right)_w$; and $W_2 = \left(\frac{\partial f_2}{\partial w}\right)_z$

which includes

$$J\,[f_1\,(x,y),\,z] = X_1\,J\,(x,\,z) + Y_1\,J\,(y,\,z) \quad \ldots \quad (7)$$

and

$$J\,[f_1\,(x,y), f_2\,(x,y)] = (X_1\,Y_2 - X_2\,Y_1)\,J\,(x,y) \quad \ldots \quad (8)$$

It follows that

$$J\,[f_1\,(x_1,\,x_2,\,\ldots\,x_n), f_2\,(y_1,\,y_2,\,\ldots\,y_n)] \quad \ldots \quad (9)$$

may be resolved by successive applications of these procedures, provided each of the variables is a function of α and β, and f_1 and f_2 are specified.

The following simple special cases of some of the above, are frequently required quickly :—

$$J\,(\alpha,\,\beta) = -J\,(\beta,\,\alpha) = 1 \quad \ldots \quad (10)$$

$$J\,(x,\,x) = J\,(k,\,x) = 0, \text{ where } k \text{ is a constant} \quad \ldots \quad (11)$$

$$J\,(x,y) = J\,(y,\,-x) = J\,(-y,\,x) = -J\,(y,\,x) \quad \ldots \quad (12)$$

$$J\,(k_1\,x,\,k_2\,y) = k_1\,k_2\,J\,(x,y) \quad \ldots \quad (13)$$

$$J\,(x^2,y) = 2x\,J\,(x,y) \quad \ldots \quad (14)$$

$$J\,(x^n,y^m) = nm\,x^{n-1}\,y^{m-1}\,J\,(x,y) \quad \ldots \quad (15)$$

$$J\,(1/x,\,1/y) = J\,(x,y)/x^2\,y^2 \quad \ldots \quad (16)$$

$$J\,(1/x,y) = J\,(y,\,x)/x^2 \quad \ldots \quad (17)$$

$$J\,(\log x,y) = J\,(x,y)/x = -y\,J\,(\log y,\,x)/x \quad \ldots \quad (18)$$

$$J\,(x+y,\,z+w) = J\,(x,\,z) + J\,(x,\,w) + J\,(y,\,z) + J\,(y,\,w) \quad \ldots \quad (19)$$

$$J\,(xy,\,zw) = xz\,J\,(y,\,w) + xw\,J\,(y,\,z) + yz\,J\,(x,\,w) + yw\,J\,(x,\,z) \quad . \quad (20)$$

$$J\,(xy,\,z) = x\,J\,(y,\,z) + y\,J\,(x,\,z) \quad \ldots \quad (21)$$

$$J\,(xy,\,x+y) = (y-x)\,J\,(x,y) \quad \ldots \quad (22)$$

$$J\,(x/y,\,z) = \{x\,J\,(z,y) - y\,J\,(z,\,x)\}/y^2 \quad \ldots \quad (23)$$

$$J\,(x/y,\,x) = x\,J\,(x,y)/y^2 \quad \ldots \quad (24)$$

$$J\,(x/y,y) = J\,(x,y)/y = -J\,(\log y,\,x) \quad \ldots \quad (25)$$

$$J\,(x/y,\,z/w) = \{xz\,J\,(y,\,w) + yw\,J\,(x,\,z) + wx\,J\,(z,y) + zy\,J\,(w,\,x)\}\,/y^2w^2 \quad \ldots \quad (26)$$

$$J\,(x,\,y) = J\,(xy,y)/y = J\,(xy,\,x)/x = J\,(x+y,y) = -J\,(x+y,\,x)$$
$$= xy\,J\,(\log x,\,\log y) = J\left\{\int f_1\,(x)\,dx,\,\int f_2\,(y)\,dy\right\}\Big/f_1\,(x)\,.\,f_2\,(y) \quad (27)$$

The following are useful in dealing with transformations of partial second derivatives :—

$$J[J(x, \alpha), \beta] = J[J(x, \beta), \alpha] \quad . \quad . \quad . \quad . \quad . \quad (28)$$

$$J[J(x, y), z] = J[J(x, z), y] + J[J(z, y), x] \quad . \quad . \quad . \quad . \quad (29)$$

$$= J[J(x, y), \alpha] \cdot J(z, \beta) - J[J(x, y), \beta] \cdot J(z, \alpha) \quad . \quad . \quad . \quad (30)$$

$$= \{J[J(x, y), x] \cdot J(z, y) - J[J(x, y), y] \cdot J(z, x)\}/J(x, y) \quad (31)$$

$$= X_1 J(x, z) + Y_1 J(y, z) \quad [\text{X and Y used as in (6)}] \quad . \quad (32)$$

$$J[J(x, y), y] = X_1 J(x, y) \quad . \quad . \quad . \quad . \quad . \quad (33)$$

$$J[J(x, y), x] = -Y_1 J(x, y) \quad . \quad . \quad . \quad . \quad . \quad (34)$$

(*Note*—The symbols Y_1 and Z_2 used in this section are defined after equation (6), and must not be confused with their use elsewhere as defined in Section 19, and Tables II, III and IV.)

11—*First and Second Partial Derivatives Expressed in Terms of Simple Jacobians*

(*a*) *First Derivatives*

If

$$\frac{\partial(x, z)}{\partial(y, w)} = \left(\frac{\partial x}{\partial y}\right)_w \cdot \left(\frac{\partial z}{\partial w}\right)_y - \left(\frac{\partial z}{\partial y}\right)_w \cdot \left(\frac{\partial x}{\partial w}\right)_y,$$

and each of the variables is some function of α and β, it can be seen by comparison with equation (1), that

$$\frac{\partial(x, z)}{\partial(y, w)} = \frac{\partial(x, z)}{\partial(\alpha, \beta)} \Big/ \frac{\partial(y, w)}{\partial(\alpha, \beta)} = \frac{J(x, z)}{J(y, w)},$$

and, therefore, that

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{\partial(x, z)}{\partial(y, z)} = \frac{J(x, z)}{J(y, z)}, \quad . \quad . \quad . \quad . \quad . \quad (35)$$

in which any desired pair of permissible variables may be substituted for α and β, when the ratio is evaluated or transformed.

(*b*) *Second Derivatives*

The most general form of partial second derivative, involves five variables, and if each of these is a function of α and β, we have

$$\left[\frac{\partial}{\partial w}\left(\frac{\partial x}{\partial y}\right)_z\right]_r = \frac{J\left[\dfrac{J(x, z)}{J(y, z)}, r\right]}{J(w, r)},$$

and referring to equation (23) we find that this becomes

$$= \frac{J(y, z) \cdot J[J(x, z), r] - J(x, z) \cdot J[J(y, z), r]}{J(w, r) \cdot [J(y, z)]^2} \quad . \quad . \quad . \quad (36)$$

If $w = y$, and $r = z$ we have the simpler case,

$$\left(\frac{\partial^2 x}{\partial y^2}\right)_z = \frac{J(y, z) \cdot J[J(x, z), z] - J(x, z) \cdot J[J(y, z), z]}{[J(y, z)]^3} . \quad . \quad . \quad (37)$$

Similarly, putting $w = z$, and $r = y$, we have

$$\frac{\partial^2 x}{\partial z \cdot \partial y} = \frac{J(y, z) \cdot J[J(x, z), y] - J(x, z) \cdot J[J(y, z), y]}{-[J(y, z)]^3} . \quad . \quad . \quad . \quad (38)$$

In the same manner, we may evaluate those second derivatives which involve four variables.

It will be noted that the procedure of equation (38) gives

$$\frac{\partial^2 x}{\partial y \cdot \partial z} = \frac{J(y, z) \cdot J[J(y, x), z] - J(y, x) \cdot J[J(y, z), z]}{[J(y, z)]^3} . \quad . \quad . \quad . \quad (39)$$

The right-hand side of (38) may be transformed into the right-hand side of (39) by the use of equations (29) and (31), yielding the well known

$$\frac{\partial^2 x}{\partial y \cdot \partial z} = \frac{\partial^2 x}{\partial z \cdot \partial y},$$

the alternative assumption of which, conversely, gives the quickest derivation of equations (28)–(31).

When representing second derivatives in this type of work it should be noted that the expression

$$\frac{\partial^2 x}{\partial y \cdot \partial z} = \frac{\partial^2 x}{\partial y_z \cdot \partial z_y} = \left[\frac{\partial}{\partial y}\left(\frac{\partial x}{\partial z}\right)_y\right]_z = \text{etc., as in (39)}$$

must not be confused with, nor equated to,

$$\frac{\partial^2 x}{\partial y_w \cdot \partial z_r} = \left[\frac{\partial}{\partial y}\left(\frac{\partial x}{\partial z}\right)_r\right]_w,$$

which is similar in type to (36).

12—*Relations which are a Consequence of the Existence of an Equation of State containing Three Variables*

If $f(x, y, z) = 0$, where any one variable is completely determined by the other two, it follows that each variable may be expressed as a function of two independent variables, α and β, and it may be shown, therefore, that

$$J(x, y)\, dz + J(y, z)\, dx + J(z, x)\, dy = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

This enables us to determine many relations between derivatives, whether the form of $f(x, y, z)$ is known or not. It should be noted first that the familiar expressions for dx, dy and dz, may be obtained by inspection of (40). For example, the following may be read, without need of re-writing,

$$dx = -\frac{J(z, x)}{J(y, z)}\,dy - \frac{J(x, y)}{J(y, z)}\,dz$$
$$= (\partial x/\partial y)_z\,dy + (\partial x/\partial z)_y\,dz,$$

and similarly for dy and dz.

If w is any function of α and β, it follows from (40) that

$$J(x, y) \,.\, J(z, w) + J(y, z) \,.\, J(x, w) + J(z, x) \,.\, J(y, w) = 0. \quad . \quad . \quad (41)$$

This compact relation is most inclusive, and with its aid the majority of transformations of partial first derivatives can be effected simply and quickly. It will be observed that the important relation, (4), follows at once by rearrangement; putting $z = \alpha$, and $w = \beta$, (41) reduces to (2) or (3); in fact, by simple substitutions and rearrangements, relations (1) to (32) may all be deduced progressively from (41).

It is obvious that by means of this equation, we may express any one $J(r, s)$ in terms of five others, provided that each variable is completely determined by any chosen two which are independent. If α and β are chosen from among the variables included in the expression (41), we find, since $J(\alpha, \beta) = 1$, that any one $J(r, s)$ may be expressed in terms of four others; this is equivalent to saying that any one ratio of two Jacobians in (41) (and thus any partial first derivative) is expressible in terms of four others.

If any other relation is known and α and β are specified, then only three independent Jacobians will be required, and any $J(r, s)$ whatever, may be expressed in terms of any three independent Jacobians with the aid of equation (41), applied successively if more than four variables are involved. Thus the foundation and the reason for the elasticity of our simple tables becomes at once apparent. If we have n variables (each functions of α and β), then with the aid of (41) and one other relation, we can automatically and very simply express any one of the $n(n-1)(n-2)$ possible partial first derivatives in terms of any three which are independent; thus we may derive, as required, a large multitude of relations each connecting a group of not more than four of the $n(n-1)(n-2)$ first derivatives (or more generally, of not more than four of the possible $n(n-1)^2(n-2)$ ratios of Jacobians, excluding ratios equal to 0 or ∞.)

If we use p, v, T and S for x, y, z and w, we have then a powerful inclusive formula in

$$J(p, v) \,.\, J(T, S) + J(v, T) \,.\, J(p, S) + J(T, p) \,.\, J(v, S) = 0 \quad . \quad . (42)$$

and any variable in this expression may be replaced by any new variable which is a function of any two of them, yielding as many equations as there are ways of choosing four different permissible variables. There are indeed available an infinite number of such equations, as we may substitute any four functions, whatever, of α and β—and α and β may be any two of any three variables, whatever, of which it may be said in turn that any two completely determine the value of the third.

13—*The Additional Relation Derived from* $dQ = dE + dW$. *Derivation of* $b^2 + ac - ln = 0$

In applying these methods in the thermodynamics of a simple substance we find several expressions of the type $zdw - xdy$ which are complete differentials, any one of which may be taken as the additional relation mentioned in the last section; the others may be deduced from it and from the relations embodied in (41).

If $zdw - xdy$ is a complete differential it follows that $J(z, w) = J(x, y)$, which, it will be noted, is not only much easier to handle and remember than the more familiar $(\partial z/\partial y)_w = -(\partial x/\partial w)_y$, but includes as many relations as there are permissible values of α and β. In this case equation (41) would reduce to

$$[J(x, y)]^2 + J(y, z) \cdot J(x, w) + J(x, z) \cdot J(y, w) = 0 \quad . \quad . \quad (43)$$

If we consider the simple cases when $dE = dQ - dW$ becomes $dE = TdS - pdv$, we have, as above

$$J(T, S) = J(p, v) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

From this we can read by inspection, any one of the MAXWELL relations merely by substituting for α and β. This is another minor illustration of the mnemonic value and saving of time obtained by using Jacobians instead of partial derivatives. (In reading these the α and β are visualized below and the desired relation read at once, for example, putting $\alpha = p$ and $\beta = S$, we visualize

$$\frac{\partial(T, S)}{\partial(p, S)} = \frac{\partial(p, v)}{\partial(p, S)} \text{ and hence } \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial v}{\partial S}\right)_p,$$

and similarly for the five others, without need of derivation or other reference).

Putting

$$\left.\begin{aligned} a &= J(v, T) \\ b &= J(p, v) = J(T, S) \\ c &= J(p, S) \\ l &= J(p, T) \\ n &= J(v, S) \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

we have from (42) the fundamental equation which is used so frequently in connection with the tables, namely,

$$b^2 + ac - ln = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

The respective meanings of a, b, c, l, and n can be recalled very simply, by visualizing

$$\left.\begin{array}{l} \mathrm{J}\,(p, v)\,.\,\mathrm{J}\,(\mathrm{T}, \mathrm{S}) + \mathrm{J}\,(v, \mathrm{T})\,.\,\mathrm{J}\,(p, \mathrm{S}) + \mathrm{J}\,(\mathrm{T}, p)\,.\,\mathrm{J}\,(v, \mathrm{S}) = 0 \\ (\;\; b \;\;)\,.\,(\;\; b \;\;) + (\;\; a \;\;)\,.\,(\;\; c \;\;) - (\;\; l \;\;)\,.\,(\;\; n \;\;) = 0 \end{array}\right\} \quad . \quad (46\mathrm{A})$$

Referring to the construction of Table I, it is apparent, that the recollection of (42) and (46) together with $d\mathrm{E} = \mathrm{T}d\mathrm{S} - pdv$, and the definition of other variables used, is sufficient to enable the whole table to be constructed rapidly, if it is not available when wanted. The parts of Table I required in most problems may indeed be recaptured and a problem solved, in only one or two minutes.

By the use of the tables (or these methods *ab initio*) any partial derivative can thus be expressed in terms of a, b, c, l and n. The choice of α and β reduced these five to four, and equation (46) reduces them to three. If desired, these three can be re-expressed in terms of any three others specially chosen (as illustrated in Sections 6 and 7), and thus, rapid transformations can be effected for even the most complicated expressions involving sets of reference derivatives in which the pairs of independent variables may, or may not, be different. No other procedure or tables have been found available which do this so simply, no matter how complicated the expression nor how diverse the choice of reference derivatives.

14—*Transformations and Use of Tables Involving* J [J (x, y), z]

It has been pointed out that Jacobians of the type J [J (x, y), z] arise in applying these methods to partial second derivatives. Under the same conditions which lead to the important equation (41), it may readily be shown that any partial second derivative is, in general, expressible in terms of not more than any four independent Jacobians of this type, and any three of the simple type, J (x, y). The object of preparing Tables III and IV is thus quite clear, and the use of these tables will be explained in Part III. In the preparation of them, however, further relations are found useful, and the calculations of the equivalent expressions cannot be made simply and quickly, as in the case of Table I.

In verifying the details of Tables III and IV it should be noted that the following form of (41) is useful, where $-\mathrm{J}\,(x, y)$ replaces w,

$$\mathrm{J}\,(x,y)\,.\,\mathrm{J}[\mathrm{J}\,(x,y), z] + \mathrm{J}\,(y, z)\,\mathrm{J}\,[\mathrm{J}\,(x,y), x] + \mathrm{J}\,(z, x)\,.\,\mathrm{J}\,[\mathrm{J}\,(x,y), y] = 0 \quad (47)$$

Also since $x = f(\alpha, \beta)$, we have $\partial^2 x/\partial\alpha\,.\,\partial\beta = \partial^2 x/\partial\beta\,.\,\partial\alpha$ giving relation (28), and similarly for y, z, etc., and we may by using (3) and (28), successively, obtain

$$\mathrm{J}\,[\mathrm{J}\,(x, y), z] + \mathrm{J}\,[\mathrm{J}\,(y, z), x] + \mathrm{J}\,[\mathrm{J}\,(z, x), y] = 0 \quad . \; . \; . \; . \; . \quad (48)$$

which leads to (29), (30) and (31) as listed before.

It will be observed that (48) is of special importance and that it may easily be recalled by noting the cyclic order. This expression is a special case of the well-known similar relation between Poisson brackets.

15—*Further Elementary Applications*

1—In elementary texts many lines are often devoted to the proofs of such relations as :—

$$\left(\frac{\partial x}{\partial z}\right)_y \cdot \left(\frac{\partial y}{\partial x}\right)_z \cdot \left(\frac{\partial z}{\partial y}\right)_x = -1 \text{ ; and } \left(\frac{\partial x}{\partial z}\right)_w \cdot \left(\frac{\partial y}{\partial x}\right)_w \cdot \left(\frac{\partial z}{\partial y}\right)_w = +1.$$

Expressed in terms of simple Jacobians, such relations may usually be obtained immediately by inspection ; for example, the two above may be read as below (without need of re-writing), and the obvious cancellations give the relations :

$$\frac{J(x, y) \cdot J(y, z) \cdot J(z, x)}{J(z, y) \cdot J(x, z) \cdot J(y, x)} = (-1)^3 = -1 \text{ ; and } \frac{J(x, w) \cdot J(y, w) \cdot J(z, w)}{J(z, w) \cdot J(x, w) \cdot J(y, w)} = +1.$$

We see by inspection, for example, in the same way, that

$$\left(\frac{\partial x_1}{\partial x_3}\right)_{x_2} \cdot \left(\frac{\partial x_2}{\partial x_4}\right)_{x_3} \cdot \left(\frac{\partial x_3}{\partial x_5}\right)_{x_4} \cdots\cdots \left(\frac{\partial x_{n-2}}{\partial x_n}\right)_{x_{n-1}} \cdot \left(\frac{\partial x_{n-1}}{\partial x_1}\right)_{x_n} \cdot \left(\frac{\partial x_n}{\partial x_2}\right)_{x_1} = (-1)^n,$$

provided each of the variables is a function of α and β.

2—If y is always constant when z is constant, then $J(x, y) = \frac{dy}{dz} \cdot J(x, z)$, since $\frac{dy}{dx} = \left(\frac{\partial y}{\partial z}\right)_r$, where r may be any variable other than y or z. An application to the case of vapours "kept saturated," has been given in Section 8. In dealing with radiation we have another example in

$$J\left(x, \frac{E}{v}\right) = \frac{d\left(\frac{E}{v}\right)}{dp} \cdot J(x, p),$$

where x is any permissible variable.

3—In using the tables in special cases when variables other than the listed ones are involved, the procedure of applying equation (6), or one of its simpler forms already enumerated, is in general necessary. It is, however, convenient to note some permanent reference relations when such cases arise, in order to avoid repetition and save time.

For example, if *density* measurements are involved, it is noted at once that

$$J(\rho, x) = -J(v, x)/v^2 \text{ or } J(v, x) = -J(\rho, x)/\rho^2,$$

where ρ is the density and x is any permissible variable referring to unit mass of a simple substance. (If dealing with a mass M, it is obviously necessary to replace $1/v^2$ by M/v^2 and $1/\rho^2$ by M/ρ^2 at the right hand of each of these expressions.)

Or again, if dealing with the *fugacity*, f, or the *activity*, $\bar{a}$, it is easily seen that

$$J(f, T) = fJ(G, T)/RT = vfJ(p, T)/RT$$

and

$$J(\bar{a}, T) = \bar{a}J(G, T)/RT = v\bar{a}J(p, T)/RT.$$

As these quantities are useful mainly in isothermal operations, in which the above would arise, it is not usually necessary to appeal to the general relation

$$\mathrm{J}\,(\mathrm{G}, x) - \mathrm{RT}\,.\,\mathrm{J}\,(\log f, x) + \mathrm{R}\log f\,.\,\mathrm{J}\,(\mathrm{T}, x) + \mathrm{J}\,(\mathrm{F}\,(\mathrm{T}), x) = 0,$$

where x is any permissible variable, and the unspecified F (T) = G − RT . log f would require to be determined independently. (The F in F (T) means "some function of.")

4—Integration for the evaluation of x in J (x, y) may be performed rapidly whenever it is possible to express J (x, y) in the form f (X) . J (X, y), where X is any function of α and β and when $\int f(\mathrm{X})\,d\mathrm{X}$ is known. Thus x is given by $\int f(\mathrm{X})\,d\mathrm{X} + k$. Similarly if

$$\mathrm{J}\,(x, y) = f_1\,(\mathrm{X}_1)\,\mathrm{J}\,(\mathrm{X}_1, y) + f_2\,(\mathrm{X}_2)\,\mathrm{J}\,(\mathrm{X}_2, y) + \ldots, \text{ etc.,}$$

we have

$$x = \int f_1\,(\mathrm{X}_1)\,d\mathrm{X}_1 + \int f_2\,(\mathrm{X}_2)\,d\mathrm{X}_2 + \ldots + k.$$

Or, if

$$\mathrm{J}\,(x, y) = \mathrm{J}\,(\mathrm{X}_1, y) + \mathrm{J}\,(\mathrm{X}_2, y) + \ldots, \text{ etc.,}$$

we have

$$x = \mathrm{X}_1 + \mathrm{X}_2 + \ldots + k.$$

For example, if $d\mathrm{E} - \mathrm{T}d\mathrm{S} + p\,dv = 0$, and $\mathrm{E} = \frac{3}{2}pv = \frac{3}{2}\mathrm{RT}$, then we should begin by considering

$$\tfrac{3}{2}\mathrm{RJ}\,(\mathrm{T}, x) - \mathrm{TJ}\,(\mathrm{S}, x) + p\mathrm{J}\,(v, x) = 0,$$

where x is any permissible variable, and hence obtain

$$\mathrm{J}\,(\tfrac{3}{2}\mathrm{R}\log\mathrm{T}, x) - \mathrm{J}\,(\mathrm{S}, x) + \mathrm{J}\,(\mathrm{R}\log v, x) = 0.$$

Therefore, it follows that

$$\tfrac{3}{2}\,\mathrm{R}\log\mathrm{T} - \mathrm{S} + \mathrm{R}\log v = k$$

which is the familiar

$$\mathrm{S} - \mathrm{S}_0 = \mathrm{R}\log\,(\mathrm{T}^{3/2}\,v/\mathrm{T}_0^{\,3/2}\,v_0)$$

for a perfect gas.

Part III—The Transformation of Partial Second Derivatives, and the Determination of Relations between them

16—*Transformations of Partial Second Derivatives. Interpretation of Table III*

Any partial second derivative may be expressed in terms of not more than four "reference second derivatives," and not more than three "reference first derivatives," provided that each variable in these derivatives is a function of α and β.

Owing to the greater complexity of second derivatives, it is convenient in making transformations, first to express all second derivatives in terms of a, b, c, Y_1, Y_2, Y_3, Y_4, in which $\alpha = p$ and $\beta = T$. Subsequent relations may then be determined in a manner similar to that employed in Sections 6 and 7. If it is desired to transform rapidly any second partial derivative into others containing pairs of independent variables other than p and T, Table III or its equivalent is essential. (The method of compiling this table requires the use of Table IV, as explained in Section 18.) If in the meantime we accept the validity of its entries, its interpretation is for the most part self-evident. In the lower left-hand corner is a summary of the meanings of the symbols, when α and β are *unspecified*.

In the upper part, the first column gives a set of seven reference derivatives when p and T are independent variables. In terms of these, any partial second derivative may be expressed with the aid of equation (36) or its equivalent.

The respective values of these derivatives in terms of Jacobians is given in the second column.

The remaining columns give the resultant expressions for the various choices of independent variables indicated at the top of each column. Throughout the upper part of the table, expressions in any one row are equal to each other, when the values given in the key lists at the foot of each column are substituted, respectively. It should be observed carefully that the meaning in each column is limited by the value of α and β at the top: thus from the table we find that

$$(a \text{ when } \alpha = p \text{ and } \beta = T) = (1/l \text{ when } \alpha = v \text{ and } \beta = T)$$
$$= [(nl - b^2)/l \text{ when } \alpha = p \text{ and } \beta = S] = \text{etc.}$$

or $(-Y_2 \text{ when } \alpha = p \text{ and } \beta = T) = [(-lZ_2 + bZ_3)/l^3 \text{ when } \alpha = v \text{ and } \beta = T] = \text{etc.}$,

where the special meaning of each symbol in terms of partial derivatives, changes from column to column, as listed at the bottom. The reason for this is obvious, and the derivation of these equivalents is consistent and simple.

Thus we read from the table that

$$[a]_{\substack{\alpha=p\\ \beta=T}} = \frac{J(v,\, T)}{J(p,\, T)} = \frac{a}{l} = \left(\frac{1}{l} \text{ when } a = 1\right) = \left(\frac{nl - b^2}{l} \text{ when } c = 1\right) \text{ etc.}$$

$$[-Y_2]_{\substack{\alpha=p\\ \beta=T}} = -J\left[\frac{J(b,\, T)}{J(p,\, T)},\, T\right] \Big/ J(p, T) = -[-lJ(b, T) + bJ(l, T)]/l^3 \text{ for all choices of } \alpha \text{ and } \beta$$

$$= (-lZ_2 + bZ_3)/l^3 \text{ when } \alpha = v \text{ and } \beta = T$$

$$= (-l^2R_1 + b^2R_2 - 2bl\,R_4)/l^3 \text{ when } \alpha = p \text{ and } \beta = S\,; \text{ etc.}$$

The verification of transformations such as the latter two is explained in Section 18.

TABLE III—TRANSFORMATIONS FROM ONE I

	In terms of J's for all permissible values of α and β	If $\alpha = p$ and $\beta = \mathrm{T}$	
$(dv/\partial p)_{\mathrm{T}} =$	$\mathrm{J}(v, \mathrm{T})/\mathrm{J}(p, \mathrm{T}) = a/l =$	a	
$(\partial v/\partial \mathrm{T}_p) =$	$\mathrm{J}(v, p)/\mathrm{J}(\mathrm{T}, p) = b/l =$	b	
$(\partial \mathrm{S}/\partial \mathrm{T})_p =$	$\mathrm{J}(\mathrm{S}, p)/\mathrm{J}(\mathrm{T}, p) = c/l =$	c	
$(\partial^2 v/\partial p^2)_{\mathrm{T}} =$	$[l\mathrm{J}(a, \mathrm{T}) - a\mathrm{J}(l, \mathrm{T})]/l^3 =$	Y_1	
$(\partial^2 \mathrm{S}/\partial p^2)_{\mathrm{T}} =$	$[-l\mathrm{J}(b, \mathrm{T}) + b\mathrm{J}(l, \mathrm{T})]/l^3 =$	$-\mathrm{Y}_2$	
$(\partial^2 v/\partial \mathrm{T}^2)_p =$	$[-l\mathrm{J}(b, p) + b\mathrm{J}(l, p)]/l^3 =$	$-\mathrm{Y}_3$	(−
$(\partial^2 \mathrm{S}/\partial \mathrm{T}^2)_p =$	$[-l\mathrm{J}(c, p) + c\mathrm{J}(l, p)]/l^3 =$	$-\mathrm{Y}_4$	$(3bl^2\mathrm{Z}$
$\partial(v, \mathrm{S})/\partial(p, \mathrm{T}) =$	$\mathrm{J}(v, \mathrm{S})/\mathrm{J}(p, \mathrm{T}) = n/l =$	$b^2 + ac = n$	

$= \mathrm{J}(v, \mathrm{T})$ $= \mathrm{J}(p, v) = \mathrm{J}(\mathrm{T}, \mathrm{S})$ $= \mathrm{J}(p, \mathrm{S})$ $= \mathrm{J}(p, \mathrm{T})$ $= \mathrm{J}(v, \mathrm{S})$ $_p = \mathrm{T}c/l$ $_v = \mathrm{T}n/a$	$\mathrm{Y}_1 = \mathrm{J}(a, \mathrm{T})$ $\mathrm{Y}_2 = \mathrm{J}(b, \mathrm{T})$ $\mathrm{Y}_3 = \mathrm{J}(b, p)$ $\mathrm{Y}_4 = \mathrm{J}(c, p)$ $\mathrm{Y}_5 = \mathrm{J}(a, p)$ $\mathrm{Y}_6 = \mathrm{J}(c, \mathrm{T})$	$\mathrm{Z}_1 = \mathrm{J}(b, v)$ $\mathrm{Z}_2 = \mathrm{J}(b, \mathrm{T})$ $\mathrm{Z}_3 = \mathrm{J}(l, \mathrm{T})$ $\mathrm{Z}_4 = \mathrm{J}(n, v)$ $\mathrm{Z}_5 = \mathrm{J}(l, v)$ $\mathrm{Z}_6 = \mathrm{J}(n, \mathrm{T})$	$a = (\partial v/\partial p)_{\mathrm{T}}$ $b = (\partial v/\partial \mathrm{T})_p = -(\partial \mathrm{S}/\partial p)_{\mathrm{T}}$ $c = (\partial \mathrm{S}/\partial \mathrm{T})_p$ $l = 1$ $n = b^2 + ac = \partial(v, \mathrm{S})/\partial(p, \mathrm{T})$ $\mathrm{Y}_1 = (\partial^2 v/\partial p^2)_{\mathrm{T}}$ $\mathrm{Y}_2 = -(\partial^2 \mathrm{S}/\partial p^2)_{\mathrm{T}} = \partial^2 v/\partial p\,.\,\partial \mathrm{T}$ $\mathrm{Y}_3 = -(\partial^2 v/\partial \mathrm{T}^2)_p = \partial^2 \mathrm{S}/\partial p\,.\,\partial \mathrm{T}$ $\mathrm{Y}_4 = -(\partial^2 \mathrm{S}/\partial \mathrm{T}^2)_p$	$a = 1$ $b = -$ $c = nl$ - $l = (\partial p$ $n = (\partial \mathrm{S}$ $\mathrm{Z}_1 = ($ $\mathrm{Z}_2 = -$ $\mathrm{Z}_3 = ($ $\mathrm{Z}_4 = -$
$_{1} = \mathrm{J}(b, \mathrm{S})$ $_{2} = \mathrm{J}(l, p)$ $_{3} = \mathrm{J}(n, \mathrm{S})$ $_{4} = \mathrm{J}(b, p)$ $_{5} = \mathrm{J}(l, \mathrm{S})$ $_{6} = \mathrm{J}(n, p)$	$\mathrm{S}_1 = \mathrm{J}(a, v)$ $\mathrm{S}_2 = \mathrm{J}(c, \mathrm{S})$ $\mathrm{S}_3 = \mathrm{J}(b, v)$ $\mathrm{S}_4 = \mathrm{J}(b, \mathrm{S})$ $\mathrm{S}_5 = \mathrm{J}(a, \mathrm{S})$ $\mathrm{S}_6 = \mathrm{J}(c, v)$	$\mathrm{M}_1 = \mathrm{J}(a, p)$ $\mathrm{M}_2 = \mathrm{J}(a, v)$ $\mathrm{M}_3 = \mathrm{J}(c, p)$ $\mathrm{M}_4 = \mathrm{J}(c, v)$ $\mathrm{M}_5 = \mathrm{J}(l, v)$ $\mathrm{M}_6 = \mathrm{J}(n, p)$	$\mathrm{N}_1 = \mathrm{J}(a, \mathrm{T})$ $\mathrm{N}_2 = \mathrm{J}(a, \mathrm{S})$ $\mathrm{N}_3 = \mathrm{J}(c, \mathrm{T})$ $\mathrm{N}_4 = \mathrm{J}(c, \mathrm{S})$ $\mathrm{N}_5 = \mathrm{J}(l, \mathrm{S})$ $\mathrm{N}_6 = \mathrm{J}(n, \mathrm{T})$	$\mathrm{Y}_5 = -\mathrm{Y}_2$ $\mathrm{Y}_6 = \mathrm{Y}_3$ $\mathrm{C}_p = \mathrm{T}c$ $\mathrm{C}_v = \mathrm{T}n/a = \mathrm{T}(b^2 + ac)/a$	$\mathrm{Z}_5 = \mathrm{Z}$ $\mathrm{Z}_6 = \mathrm{Z}$ $\mathrm{C}_p = \mathrm{T}$ $\mathrm{C}_v = \mathrm{T}$

* S_1,

Pair of Independent Variables to another; and Key to Symbols. $(b^2 + ac - ln =$

If $\alpha = v$ and $\beta = T$	If $\alpha = p$ and $\beta = S$	If $\alpha = v$ and $\beta = S$*
$1/l$	$(nl - b^2)/l$	$a/(b^2 + ac)$
b/l	b/l	$b/(b^2 + ac)$
$(nl - b^2)/l$	$1/l$	$c/(b^2 + ac)$
$- Z_3/l^3$	$(- 3bl^2 R_1 + b^3R_2 + l^3R_3 - 3b^2lR_4)/l^3$	$(b^3S_1 - a^3S_2 - 3ab^2S_3 - 3a^2bS_4)/(b^2 + ac)^3$
$(- lZ_2 + bZ_3)/l^3$	$(- l^2R_1 + b^2R_2 - 2blR_4)/l^3$	$[b^2cS_1 + a^2bS_2 + (b^3 - 2\,abc)\ S_3 + (2ab^2 - a^2c)\ S_4]/(b^2 + ac)^3$
$- l^2Z_1 + 2blZ_2 - b^2Z_3)/l^3$	$(bR_2 - lR_4)/l^3$	$[bc^2S_1 - ab^2S^2 + (2b^2c - ac^2)\ S_3 + (2abc - b^3)\ S_4]/(b^2 + ac)^3$
$Z_1 - 3b^2lZ_2 + b^3Z_3 - l^3Z_4)/l^3$	R_2/l^3	$(c^3S_1 + b^3S_2 + 3bc^2S_3 - 3b^2cS_4)/(b^2 + ac)^3$
n/l	n/l	$1/(b^2 + ac) = 1/l$
$- (\partial p/\partial T)_v = - (\partial S/\partial v)_T$ $l - b^2 = \partial(p, S)/\partial (v, T)$ $\partial p/\partial v)_T$ $\partial S/\partial T)_v$	$a = nl - b^2 = \partial (v, T)/\partial (p, S)$ $b = (\partial T/\partial p)_S = (\partial v/\partial S)_p$ $c = 1$ $l = (\partial T/\partial S)_p$ $n = (\partial v/\partial p)_S$	$a = (\partial T/\partial S)_v$ $b = (\partial T/\partial v)_S = - (\partial p/\partial S)_v$ $c = (\partial p/\partial v)_S$ $l = b^2 + ac = \partial (p, T)/\partial (v, S)$ $n = 1$
$(\partial^2p/\partial T^2)_v = \partial^2S/\partial v\ .\ \partial T$ $- (\partial^2S/\partial v^2)_T = - \partial^2p/\partial v\ .\ \partial T$ $(\partial^2p/\partial v^2)_T$ $- (\partial^2S/\partial T^2)_v$	$R_1 = (\partial^2T/\partial p^2)_S = \partial^2v/\partial p.\partial S$ $R_2 = - (\partial^2T/\partial S^2)_p$ $R_3 = (\partial^2v/\partial p^2)_S$ $R_4 = - (\partial^2v/\partial S^2)_p = - \partial^2T/\partial p\ .\ \partial S$	$S_1 = - (\partial^2T/\partial S^2)_v$ $S_2 = (\partial^2p/\partial v^2)_S$ $S_3 = (\partial^2p/\partial S^2)_v = - \partial^2T/\partial v\ .\ \partial S$ $S_4 = (\partial^2T/\partial v^2)_S = - \partial^2p/\partial v\ .\ \partial S$
Z_2 Z_1	$R_5 = - R_4$ $R_6 = - R_1$	$S_5 = - S_3$ $S_6 = S_4$
$Tc/l = T\ (nl - b^2)/l$ Tn	$C_p = T/l$ $C_v = Tn/a = Tn/(nl - b^2)$	$C_p = Tc/l = Tc\ (b^2 + ac)$ $C_v = T/a$

, S_2, S_3, S_4, S_5, and S_6 must not be confused with S, the entropy.

$c - ln = 0$ in all cases)

	If $\alpha = p$ and $\beta = v$	If $\alpha = \mathrm{T}$ and $\beta = \mathrm{S}$
	a/l	a/l
	$1/l$	$1/l$
	c/l	c/l
$+ ac)^3$	$[- a(2 + ac)\,\mathrm{M}_1 + l(1 + ac)\,\mathrm{M}_2 + a^3\mathrm{M}_3 - a^2l\mathrm{M}_4]/l^3n$	$(\mathrm{N}_1 + al\mathrm{N}_2 - a^2\mathrm{N}_3)/l^3n$
	$(\mathrm{M}_1 - a^2\mathrm{M}_3 + al\mathrm{M}_4)/l^3n$	$(c\mathrm{N}_1 - l\mathrm{N}_2 + a\mathrm{N}_3)/l^3n$
$+ ac)^3$	$(c\mathrm{M}_1 + a\mathrm{M}_3 - l\mathrm{M}_4)/l^3n$	$(c^2\mathrm{N}_1 - cl\mathrm{N}_2 - \mathrm{N}_3)/l^3n$
$+ ac)^3$ $^2 + ac)^3$	$(c^2\mathrm{M}_1 - \mathrm{M}_3 - cl\mathrm{M}_4)/l^3n$	$[c^3\mathrm{N}_1 - c^2l\mathrm{N}_2 - c - c(2 + ac)\,\mathrm{N}_3 + l(1 + ac)\,\mathrm{N}_4]/l^3n$
	$(1 + ac)/l^2 = n/l$	$(1 + ac)/l^2 = n/l$
	$a = -(\partial\mathrm{T}/\partial p)_v$ $b = 1$ $c = (\partial\mathrm{S}/\partial v)_p$ $l = (\partial\mathrm{T}/\partial v)_p$ $n = (1 + ac)/l = -(\partial\mathrm{S}/\partial p)_v$	$a = -(\partial v/\partial\mathrm{S})_\mathrm{T}$ $b = 1$ $c = (\partial p/\partial\mathrm{T})_\mathrm{S}$ $l = -(\partial p/\partial\mathrm{S})_\mathrm{T}$ $n = (1 + ac)/l = (\partial v/\partial\mathrm{T})_\mathrm{S}$
	$\mathrm{M}_1 = \partial^2\mathrm{T}/\partial p\,.\,\partial v$ $\mathrm{M}_2 = -(\partial^2\mathrm{T}/\partial p^2)_v$ $\mathrm{M}_3 = -(\partial^2\mathrm{S}/\partial v^2)_p$ $\mathrm{M}_4 = \partial^2\mathrm{S}/\partial p\,.\,\partial v$	$\mathrm{N}_1 = (\partial^2 v/\partial\mathrm{S}^2)_\mathrm{T}$ $\mathrm{N}_2 = -\partial^2 v/\partial\mathrm{T}\,.\,\partial\mathrm{S}$ $\mathrm{N}_3 = -\partial^2 p/\partial\mathrm{T}\,.\,\partial\mathrm{S}$ $\mathrm{N}_4 = (\partial^2 p/\partial\mathrm{T}^2)_\mathrm{S}$
	$\mathrm{M}_5 = \mathrm{M}_1$ $\mathrm{M}_6 = \mathrm{M}_4$	$\mathrm{N}_5 = \mathrm{N}_3$ $\mathrm{N}_6 = \mathrm{N}_2$
	$\mathrm{C}_p = \mathrm{T}c/l$ $\mathrm{C}_v = \mathrm{T}n/a = \mathrm{T}(1 + ac)/al$	$\mathrm{C}_p = \mathrm{T}c/l$ $\mathrm{C}_v = \mathrm{T}n/a = \mathrm{T}(1 + ac)/al$

To be entirely free from ambiguity it would be necessary to write each symbol in the column for $\alpha = p$ and $\beta = \mathrm{T}$, in some such form as $[x]_{\substack{\alpha=p\\ \beta=\mathrm{T}}}$ where x represents a, b, c, Y_1, Y_2, Y_3, or Y_4, wherever they occur in that particular column. Similarly in the column for $\alpha = v$ and $\beta = \mathrm{T}$, each symbol x should be $[x]_{\substack{\alpha=v\\ \beta=\mathrm{T}}}$, and so on for each column. In practice, this is, however, unnecessarily cumbersome, and may be omitted as is done in Table III, provided it is remembered that $[x]_{\substack{\alpha=x\\ \beta=y}} \neq x$; for example $[\mathrm{Y}_1]_{\substack{\alpha=p\\ \beta=\mathrm{T}}} \neq \mathrm{Y}_1$ since the actual relation is (as may be seen from Tables III and IV)

$$[\mathrm{Y}_1]_{\substack{\alpha=p\\ \beta=\mathrm{T}}} = \left[l\mathrm{Y}_1 - \frac{a}{n}\{b\,(\mathrm{Y}_2 + \mathrm{Y}_5) + a\,(\mathrm{Y}_6 - \mathrm{Y}_3)\}\right]\Big/ l^3,$$

where the right-hand side holds for all values of α and β, reducing to the single symbol Y_1, only when $\alpha = p$ and $\beta = \mathrm{T}$ which makes $l = 1$, and $\mathrm{Y}_2 + \mathrm{Y}_5 = \mathrm{Y}_6 - \mathrm{Y}_3 = 0$.

Although the explanation, and the compilation of this table may appear complicated, its actual use, will be seen to be simple and straightforward. For example :—" *Express* $(\partial^2 v/\partial \mathrm{T}^2)_p$ *in terms of derivatives, in which the independent variables are* p *and* v." The table gives the answer at once as

$$(c\mathrm{M}_1 + a\mathrm{M}_3 - l\mathrm{M}_4)/l^2\,(1 + ac),$$

where we have used $(1 + ac)/l$ for n in order to reduce the number of first derivatives to three. Filling in the values from the bottom of the column, the full expression is obtained without any analysis, namely,

$$\left[\left(\frac{\partial \mathrm{S}}{\partial v}\right)_p \cdot \frac{\partial^2 \mathrm{T}}{\partial p\,.\,\partial v} + \left(\frac{\partial \mathrm{T}}{\partial p}\right)_v \cdot \left(\frac{\partial^2 \mathrm{S}}{\partial v^2}\right)_p - \left(\frac{\partial \mathrm{T}}{\partial v}\right)_p \cdot \frac{\partial^2 \mathrm{S}}{\partial p\,.\,\partial v}\right]\Big/\left(\frac{\partial^2 \mathrm{T}}{\partial v^2}\right)_p \cdot \left\{1 - \left(\frac{\partial \mathrm{T}}{\partial v}\right)_p \cdot \left(\frac{\partial \mathrm{S}}{\partial v}\right)_p\right\}.$$

No difficulty arises in this type of transformation ; all the information is in the table ; in this case one could have used $n = -(\partial \mathrm{S}/\partial v)_p$ if desired.

The use of four of a, b, c, l and n, instead of three, in four items in the last two columns of the table is merely because, (1) there is no possibility, when $b = 1$, of the appearance of the form $\partial\,(x, y)/\partial\,(z, w)$ which has to be avoided in the other columns, and (2) the form $l^3 n$ is more compact than $l^2(1 + ac)$, and may often be used conveniently in connection with M or N transformations.

17—*Examples Illustrating the Use of Table III in Dealing with Transformations of Partial Second Derivatives*

The two following examples are chosen, arbitrarily, to illustrate the technique of applying the table.

1—*Find a relation between* $(\partial \mathrm{C}_v/\partial v)_\mathrm{T}$ *and* $(\partial \mathrm{C}_p/\partial p)_\mathrm{T}$ *which involves only derivatives containing* v *and* T *as independent variables.*

Using Tables I and III, we have

$$\left(\frac{\partial \mathrm{C}_v}{\partial v}\right)_\mathrm{T} = \frac{\mathrm{J}\,[\mathrm{T}n/a,\,\mathrm{T}]}{\mathrm{J}\,(v,\,\mathrm{T})} = \mathrm{T}\,[\mathrm{J}\,(n,\,\mathrm{T})]_{a=1} = \mathrm{T}\,[\mathrm{Z}_1]_{\substack{\alpha=v\\ \beta=\mathrm{T}}}$$

and

$$\left(\frac{\partial C_p}{\partial p}\right)_T = \frac{J(Tc/l, T)}{J(p, T)} = T[J(c, T)]_{l=1} = T[Y_3]_{\substack{\alpha=p\\ \beta=T}}$$

and, as shown by Table III, the latter becomes

$$\left(\frac{\partial C_p}{\partial p}\right)_T = T[Y_3]_{l=1} = T\left[\frac{l^2Z_1 - 2blZ_2 + b^2Z_3}{l^3}\right]_{\substack{\alpha=v\\ \beta=T}}.$$

Hence using the above value of $(\partial C_v/\partial v)_T$ and substituting from the lower part of the Z column in Table III, we get the desired relation, namely,

$$\left(\frac{\partial C_p}{\partial p}\right)_T = \frac{\left(\frac{\partial p}{\partial v}\right)_T^2 \cdot \left(\frac{\partial C_v}{\partial v}\right)_T - 2T\left(\frac{\partial p}{\partial T}\right)_v \cdot \left(\frac{\partial p}{\partial v}\right)_T \cdot \frac{\partial^2 p}{\partial v \,.\, \partial T} + T\left(\frac{\partial p}{\partial T}\right)_v^2 \cdot \left(\frac{\partial^2 p}{\partial v^2}\right)_T}{\left(\frac{\partial p}{\partial v}\right)_T^3}.$$

2—*Express* $(\partial p/\partial T)_{C_p}$ *in terms of the minimum number of first and second derivatives in which the independent variables are* p *and* S.

Using Tables I and III, as in example (1) above, we have

$$\left(\frac{\partial p}{\partial T}\right)_{C_p} = \frac{J(p, Tc/l)}{J(T, Tc/l)} = \left[\frac{T\,J(p, c) + c}{TJ(T, c)}\right]_{l=1}$$

$$= \left[\frac{-TY_4 + c}{-TY_3}\right]_{l=1} = \left[\frac{T(R_2/l^3) + (1/l)}{T(bR_2 - lR_4)/l^3}\right]_{c=1}$$

$$= \left[\frac{TR_2 + l^2}{TbR_2 - TlR_4}\right]_{\substack{\alpha=p\\ \beta=S}} = \frac{-T\left(\frac{\partial^2 T}{\partial S^2}\right)_p + \left(\frac{\partial T}{\partial S}\right)_p^2}{-T\left(\frac{\partial T}{\partial p}\right)_S \cdot \left(\frac{\partial^2 T}{\partial S^2}\right)_p + T\left(\frac{\partial T}{\partial S}\right)_p \cdot \left(\frac{\partial^2 v}{\partial S^2}\right)_p}$$

(If $pv = RT$, it will be seen by the aid of Table IA that this expression reduces to $(\partial C_p/\partial T)_p/0 = \infty$, and if C_p is not a function of p and T, as in the case of an ideal monatomic gas where $C_p = 5R/2$, the expression becomes indeterminate, reducing to 0/0. In this case, these points are obvious and academic, but they are mentioned to illustrate the ease with which such questions are covered automatically by the tables.)

18—*The Interpretation of Table IV. Illustration of its Use in the Preparation of Table III*

The chief application of Table IV lies in its use in the construction of Table III, or other similar tables for handling partial second derivatives. In Table IV, there are tabulated various expressions for Jacobians, J (r, s), where r is any one of a, b, c, l, and n, and s is any one of p, v, T, and S.

Each column gives values in terms of six "reference Jacobians" of the type J [J (x, y), z], indicated by Y_1, Y_2 . . . Y_6, Z_1, Z_2 . . . Z_6, etc. These are chosen with

TABLE IV—TABLE OF ALTERNATIVE EXPRESSIONS FOR J [J (x,

(Each row consists of equivalent ex

	In terms of Y's	In terms of Z's	In terms of R's	
J (a, p)	Y_5	$Z_5 - Z_2$	$J(l, v) - J(b, T)$	
J (a, v)	$(bY_1 + aY_5)/l$	$[bJ(a, S) + nJ(a, p)]/c$	$[nJ(a, p) + bJ(a, S)]/c$	
J (a, T)	Y_1	$[lJ(a, S) + bJ(a, p)]/c$	$[bJ(a, p) + lJ(a, S)]/c$	
J (a, S)	$(cY_1 - bY_5)/l$	$Z_6 - Z_1$	$J(n, T) - J(b, v)$	
J (b, p)	Y_3	$(lZ_1 - bZ_2)/a$	R_4	
J (b, v)	$(bY_2 + aY_3)/l$	Z_1	$(nR_4 + bR_1)/c$	
J (b, T)	Y_2	Z_2	$(bR_4 + lR_1)/c$	
J (b, S)	$(cY_2 - bY_3)/l$	$(-bZ_1 + nZ_2)/a$	R_1	
J (c, p)	Y_4	$[lJ(c, v) - bJ(c, T)]/a$	$[lJ(c, v) - bJ(c, T)]/a$	
J (c, v)	$(bY_6 + aY_4)/l$	$(J(n, p) + J(b, S)$	$R_1 + R_6$	
J (c, T)	Y_6	$J(l, S) + J(b, p)$	$R_4 + R_5$	
J (c, S)	$(cY_6 - bY_4)/l$	$[nJ(c, T) - bJ(c, v)]/a$	$[nJ(c, T) - bJ(c, v)]/a$	
J (l, p)	$[cJ(l, v) - bJ(l, S)]/n$	$(lZ_5 - bZ_3)/a$	R_2	[cJ
J (l, v)	$Y_2 + Y_5$	Z_5	$(nR_2 + bR_5)/c$	J
J (l, T)	$[bJ(l, v) + aJ(l, S)]/n$	Z_3	$(bR_2 + lR_5)/c$	[bJ
J (l, S)	$Y_6 - Y_3$	$(nZ_3 - bZ_5)/a$	R_5	J
J (n, p)	$J(c, v) - J(b, S)$	$(lZ_4 - bZ_6)/a$	R_6	
J (n, v)	$[bJ(n, T) + aJ(n, p)]/l$	Z_4	$(nR_6 + bR_3)/c$	[bJ
J (n, T)	$J(a, S) + J(b, v)$	Z_6	$(bR_6 + lR_3)/c$	
J((n, S)	$[cJ(n, T) - bJ(n, p)]/l$	$(nZ_6 - bZ_4)/a$	R_3	[cJ

If $x = a, b, c, l$ or n (or any other function of α and β), we have,

$$J(x, E) = [(Tc - pb) J(x, T) - (Tb + pa) J(x, p)]/l$$
$$J(x, I) = [(Tc J(x, T) + (vl - Tb) J(x, p)]/l$$
$$J(x, F) = - [(Sl + pb) J(x, T) + paJ(x, p)]/l$$

* Note that S_1, S_2, S_3, S_4, S_5, and S_6, used in this

$y), z]$. For use in Transforming Partial Second Derivatives

expressions for the same α and β only.)

In terms of S's*	In terms of M's	In terms of N's	
$(cS_1 - bS_5)/n$ S_1 $(bS_1 + aS_5)/n$ S_5	M_1 M_2 $(-aM_1 + lM_2)/b$ $(-nM_1 + cM_2)/b$	$(cN_1 - lN_2)/b$ $(nN_1 - aN_2)/b$ N_1 N_2	$J[J(v, T), p]$ $J[J(v, T), v]$ $J[J(v, T), T]$ $J[J(v, T), S]$
$(cS_3 - bS_4)/n$ S_3 $(bS_3 + sS_4)/n$ S_4	$[cJ(b, T) - lJ(b, S)]/b$ $[nJ(b, T) - aJ(b, S)]/b$ $M_5 - M_1$ $M_4 - M_6$	$N_3 - N_5$ $N_6 - N_2$ $[-aJ(b, p) + lJ(b, v)]/b$ $[-nJ(b, p) + cJ(b, v)]/b$	$J[J(p, v), p] = J[J($ $J[J(p, v), v] = J[J($ $J[J(p, v), T] = J[J($ $J[J(p, v), S] = J[J($
$(cS_6 - bS_2)/n$ S_6 $(bS_6 + aS_2)/n$ S_2	M_3 M_4 $(-aM_3 + lM_4)/b$ $(-nM_3 + cM_4)/b$	$(cN_3 - lN_4)/b$ $(nN_3 - aN_4)/b$ N_3 N_4	$J[J(p, S), p]$ $J[J(p, S), v]$ $J[J(p, S), T]$ $J[J(p, S), S]$
$cJ(l, v) - bJ(l, S)]/n$ $J(b, T) + J(a, p)$ $bJ(l, v) + aJ(l, S)]/n$ $J(c, T) - J(b, p)$	$[cJ(l, v) - bJ(l, S)]/n$ M_5 $[bJ(l, v) + aJ(l, S)]/n$ $J(c, T) - J(b, p)$	$[cJ(l, v) - bJ(l, S)]/n$ $J(b, T) + J(a, p)$ $[bJ(l, v) + aJ(l, S)]/n$ N_5	$J[J(p, T), p]$ $J[J(p, T), v]$ $J[J(p, T), T]$ $J[J(p, T), S]$
$S_6 - S_4$ $bJ(n, T) + aJ(n, p)]/l$ $S_3 + S_5$ $J(n, T) - bJ(n, p)]/l$	M_6 $[aJ(n, p) + bJ(n, T)]/l$ $J(a, S) + J(b, v)$ $[-bJ(n, p) + cJ(n, T)]/l$	$J(c, v) - J(b, S)$ $[aJ(n, p) + bJ(n, T)]/l$ N_6 $[-bJ(n, p) + cJ(n, T)]/l$	$J[J(v, S), p]$ $J[J(v, S), v]$ $J[J(v, S), T]$ $J[J(v, S), S]$

$$J(x, G) = -SJ(x, T) + vJ(x, p)$$
$$J(x, Q) = [TcJ(x, T) - TbJ(x, p)]/l$$
$$J(x, W) = [pbJ(x, T) + paJ(x, p)]/l$$

is column, must not be confused with S, the entropy.

, T), p]
, T), v]
, T), T]
, T), S]
= J [J (T, S), p]
= J [J (T, S), v]
= J [J (T, S), T]
= J [J (T, S), S]
, S), p]
, S), v]
, S), T]
, S), S]
, T), p]
, T), v]
, T), T]
, T), S]
, S), p]
, S), v]
, S), T]
, S), S]

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

reference to the subsequently required sets of "reference second derivatives," which vary in convenience of use depending upon which of a, b, c, l, and n is equal to unity. It will be observed that whenever Jacobians are mentioned inside these columns, they may in each case be resolved with the aid of the rest of the column; they are written in this form only to save space; for example, in the Y column,

$$J(n, p) = J(c, v) - (Jb, S) = (bY_6 + aY_4)/l - (cY_2 - bY_3)/l$$

which can be read from the table without auxiliary calculation.

It will be found that the expressions in any one horizontal row in the table, are identically equal to each other, *provided that* α *and* β *remain the same, or are unspecified.*

When, in application to second derivatives, some definite values are assigned to α and β, it will be observed that the number of new independents are reduced from six to four in each column; for example, if $\alpha = p$ and $\beta = T$, then $l = 1$, and $J(l, x) = 0$, hence $Y_5 = -Y_2$ and $Y_6 = Y_3$. Similarly if $\alpha = v$, and $\beta = T$, we find $Z_5 = Z_2$ and $Z_6 = Z_1$, and so on, as shown near the foot of Table III.

It is unnecessary to demonstrate the tedious detail of filling in Table IV; it will be found that this can be done with the aid of the transformations given in Section 10.

The construction of the more useful Table III, is a lengthy process. It may be illustrated by calculating one typical item. Consider, for example, the seventh item in the fourth column of Table III where the Z's appear. We have to show that :—

$$(-Y_4 \text{ in the particular case when } \alpha = p \text{ and } \beta = T)$$

is equal to

$$(3\,bl^2Z_1 - 3\,b^2lZ_2 + b^3Z_3 - l^3Z_4)/l^3$$

in the particular case when $\alpha = v$ *and* $\beta = T$.

It will be observed that, whereas $-Y_4 = -J(c, p)$ when α and β are *unspecified* either for $J(c, p)$ or for c, we find new meanings arise as soon as α and β are specified. Thus we have

$$[-Y_4]_{\substack{\alpha=p\\ \beta=T}} = -[J(c, p) \text{ when } \alpha = p \text{ and } \beta = T]$$

$$= -\left[J\left\{\frac{J(p, S)}{J(p, T)}, p\right\}\Big/ J(p, T) \text{ for all values of } \alpha \text{ and } \beta\right]$$

$$= -\frac{J(c/l, p)}{l} = \frac{-lJ(c, p) + cJ(l, p)}{l^3} \ldots \text{ by equation (23).}$$

where these equivalent expressions hold for all values of α, and β, reducing to $J(c, p)$ only when $\alpha = p$ and $\beta = T$, but giving any desired transformation for other choices of α and β.

To express this in terms of Z's, we turn to Table IV and then substitute the values for $J(c, p)$ and $J(l, p)$ in the above expression, thus,

$$[-Y_4]_{\substack{\alpha=p\\ \beta=T}} = \left[-\frac{l}{a}\left\{l\left(\frac{lZ_4 - bZ_6}{a} + \frac{-bZ_1 + nZ_2}{a}\right) - b\left(\frac{nZ_3 - bZ_5}{a} + \frac{lZ_1 - bZ_2}{a}\right)\right\} + \frac{c}{a}\{lZ_5 - bZ_3\}\right]\Big/ l^3.$$

Now this is true for all values of α and β, but we desire the special case, $\alpha = v$ and $\beta = T$, that is, when $a = 1$; under these conditions $Z_5 = Z_2$ and $Z_6 = Z_1$, also $c = nl - b^2$; substituting these values, we find that the above expression reduces to

$$[-Y_4]_{\substack{\alpha=p\\ \beta=T}} = \left[\frac{3\,bl^2Z_1 - 3\,b^2lZ_2 + b^3Z_3 - l^3Z_4}{l^3}\right]_{\substack{\alpha=v\\ \beta=T}},$$

as given in Table III, where $b\ l\ Z_1\ Z_2,\ Z_3\ Z_4$ are the first and second derivatives given in the lower part of the Z column.

Each item of Table III had to be determined laboriously in this manner, and was checked by an independent transformation back again via another column. It will be observed that without Table III and Table IV, the general transformations of partial second derivatives, in many cases, would be tasks each requiring several hours to perform.

19—*List of Symbols Used in this Article*

Ordinary variables:

p = the pressure.

v = the volume per unit mass.

T = the absolute temperature.

S = the entropy per unit mass. (The product TS is in the same units as pv.)

E = the internal energy per unit mass. (In the same units as the product pv.)

I = the "total heat," E + pv.

F = the thermodynamic potential at constant volume, or the "free energy" (HELMHOLTZ), E − TS.

G = the thermodynamic potential at constant pressure, or the "free energy" (G. N. LEWIS), E − TS + pv.

dQ = the heat absorbed per unit mass during an infinitesimal change. (In the same units as the product pv.)

dW = the external work done per unit mass during an infinitesimal change. (In the same units as the product pv.)

Derivatives:

C_v = the specific heat at constant volume (expressed in the same units as the product pv).

C_p = the specific heat at constant pressure (expressed in the same units as the product pv).

$p_x = (\partial T/\partial p)_x$, the "cooling effect" at constant x, where x is any one of the above variables.

$\alpha_p = (\partial v/\partial T)_p/v$, the true coefficient of cubical expansion at constant pressure.

$\kappa_T = -(\partial v/\partial p)_T/v$, the true coefficient of compressibility at constant temperature.

" *Reference Jacobians* ":

a, b, c, l, and n ;

Y_r, Z_r, R_r, S_r, M_r, N_r, where $r = 1, 2, 3, 4, 5,$ and 6.

These are all defined in the left-hand lower corner of Table III. See also Table I for a, b, c, l, and n, and Section 13 for a simple mnemonic procedure for identifying these frequently used symbols.

[*Note*—The symbols S_1, S_2, S_3, S_4, S_5, and S_6 should not be confused with S, the entropy ; Greek letters have been avoided in order to simplify the printing and no other unappropriated capital letter remained; the Jacobian S_r, are, however, required only rarely.]

Miscellaneous :

$\gamma = C_p/C_v$.

$E' = E/v$, the density of internal energy, or the density of radiation in a cavity if E is taken as the energy in a region of volume v.

L_T = Latent heat of change of state per unit mass at temperature T.

R = Gas constant for unit mass.

a' = VAN DER WAAL's constant in $(P + a'/v^2) \cdot (v - b') = RT$.

b' = VAN DER WAAL's constant in $(P + a'/v^2) \cdot (v - b') = RT$.

S' = total energy emission from a black body, per cm^2 per sec. $[E' = 4S'/(3 \times 10^{10})]$.

$e_\lambda = dS'/d\lambda$ = " emissive power " of a black body for radiation of wave-length, λ. ($e_\lambda\, d\lambda$ = the energy in waves between λ and $\lambda + d\lambda$ given off per cm^2 per sec.)

This work began as a result of using the valuable tables of Dr. P. W. BRIDGMAN, when it was desired greatly to extend their range and, if possible, to devise a simple direct procedure with a minimum of tabulation. As a result of the suggestions contained in BRIDGMAN's tables, the writer developed a simple theorem called the " *AB Theorem* " which has been discussed in " The Rapid Derivation of Thermodynamical Relations."* The application of Jacobians in an attempt to systematize and extend the use of this theorem, lead to the present work,† which now entirely supersedes the former scheme of the writer, and greatly surpasses it in range of application, compactness of tabulation, and speed of usage.

* Shaw, 'Trans. Roy. Soc. Can.,' Sect. III, vol. 26, p. 177 (1932).

† A ten minute verbal account of a few of the features in Part I was given at the annual meeting of the American Physical Society in Boston, December 28, 1933 ; another brief address (20 minutes) was given at the meeting of the Royal Society of Canada in Quebec, May 22, 1934 ; this is the first written account, no part of which has been submitted previously for publication.

The writer is also indebted to Dean A. S. EVE for his keen interest in the development of this new technique, to Dr. W. H. WATSON for several valuable suggestions, and to Dr. J. KATZMAN for assistance in tabulation. Especial thanks are due also to those Honours and Graduate Students at McGill University, who kindly assisted in demonstrating the high speed with which the new method could be learnt and applied, *ab initio*, to the derivation of large numbers of relations.

20—*Summary*

The following is a list of the main features and points of probable value in this paper :—

(1) The development of a direct procedure for rapidly expressing any first or second partial derivative (relating to a simple substance), in terms of any possible permissible set of "reference derivatives" whether the pairs of independent variables are the same in each reference derivative or not.

(2) The formulation of compact tables which enable many million thermodynamical relations to be derived simply and systematically, as required.

(3) The application of these methods to special cases, such as substances obeying a given equation of state, perfect gases, vapours kept saturated, radiation, etc.

(4) The outline of the underlying theory of the method, which rests primarily on the equations :—

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{J(x, z)}{J(y, z)}$$

$$J(T, S) - J(p, v) = 0$$

$$J(x, y) \cdot J(z, w) + J(y, z) \cdot J(w, x) + J(z, x) \cdot J(y, w) = 0$$

$$J[J(x, y), z] + J[J(y, z), x] + J[J(z, x), y] = 0$$

where x, y, z, w, are each functions of α and β. A review of procedure in transforming Jacobians, and in using them either in the construction of tables or directly in cases where the tables are not essential.

(5) The provision of detailed instructions and illustrations, so that the methods may be easily learnt, taught, or applied.

(6) The demonstration of great saving of time in solving problems, and in formulating and applying entirely new relations whenever required.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Table III—Transformations from one Pair of Independent Variables to another; and Key to Symbols. ($b^2 + ac - ln = 0$ in all cases)

	In terms of J's for all permissible values of α and β	If $\alpha = p$ and $\beta = T$	If $\alpha = v$ and $\beta = T$	If $\alpha = p$ and $\beta = S$	If $\alpha = v$ and $\beta = S$*	If $\alpha = p$ and $\beta = v$	If $\alpha = T$ and $\beta = S$
$(\partial v/\partial p)_T =$	$J(v, T)/J(p, T) = a/l =$	a	$1/l$	$(nl - b^2)/l$	$a/(b^2 + ac)$	a/l	a/l
$(\partial v/\partial T_p) =$	$J(v, p)/J(T, p) = b/l =$	b	b/l	b/l	$b/(b^2 + ac)$	$1/l$	$1/l$
$(\partial S/\partial T)_p =$	$J(S, p)/J(T, p) = c/l =$	c	$(nl - b^2)/l$	$1/l$	$c/(b^2 + ac)$	c/l	c/l
$(\partial^2 v/\partial p^2)_T =$	$[lJ(a, T) - aJ(l, T)]/l^3 =$	Y_1	$-Z_3/l^3$	$(-3bl^2 R_1 + b^3R_2$ $+ l^3R_3 - 3b^2lR_4)/l^3$	$(b^3S_1 - a^3S_2 - 3ab^2S_3$ $- 3a^2bS_4)/(b^2 + ac)^3$	$[-a(2 + ac)M_1$ $+ l(1 + ac)M_2$ $+ a^3M_3 - a^2lM_4]/l^3n$	$(N_1 + alN_2 - a^2N_3)/l^3n$
$(\partial^2 S/\partial p^2)_T =$	$[-lJ(b, T) + bJ(l, T)]/l^3 =$	$-Y_2$	$(-lZ_2 + bZ_3)/l^3$	$(-l^2R_1 + b^2R_2 - 2blR_4)/l^3$	$[b^2cS_1 + a^2bS_2 + (b^3 - 2abc)S_3$ $+ (2ab^2 - a^2c)S_4]/(b^2 + ac)^3$	$(M_1 - a^2M_3 + alM_4)/l^3n$	$(cN_1 - lN_2 + aN_3)/l^3n$
$(\partial^2 v/\partial T^2)_p =$	$[-lJ(b, p) + bJ(l, p)]/l^3 =$	$-Y_3$	$(-l^2Z_1 + 2blZ_2 - b^2Z_3)/l^3$	$(bR_2 - lR_4)/l^3$	$[bc^2S_1 - ab^2S^2 + (2b^2c - ac^2)S_3$ $+ (2abc - b^3)S_4]/(b^2 + ac)^3$	$(cM_1 + aM_3 - lM_4)/l^3n$	$(c^2N_1 - clN_2 - N_3)/l^3n$
$(\partial^2 S/\partial T^2)_p =$	$[-lJ(c, p) + cJ(l, p)]/l^3 =$	$-Y_4$	$(3bl^2Z_1 - 3b^2lZ_2 + b^3Z_3 - l^3Z_4)/l^3$	R_2/l^3	$(c^3S_1 + b^3S_2 + 3bc^2S_3 - 3b^2cS_4)/(b^2 + ac)^3$	$(c^2M_1 - M_3 - clM_4)/l^3n$	$[c^3N_1 - c^2lN_2 - c$ $- c(2 + ac)N_3$ $+ l(1 + ac)N_4]/l^3n$
$\partial(v, S)/\partial(p, T) =$	$J(v, S)/J(p, T) = n/l =$	$b^2 + ac = n$	n/l	n/l	$1/(b^2 + ac) = 1/l$	$(1 + ac)/l^2 = n/l$	$(1 + ac)/l^2 = n/l$
$a = J(v, T)$ $b = J(p, v) = J(T, S)$ $c = J(p, S)$ $l = J(p, T)$ $n = J(v, S)$	$Y_1 = J(a, T)$ $Z_1 = J(b, v)$ $Y_2 = J(b, T)$ $Z_2 = J(b, T)$ $Y_3 = J(b, p)$ $Z_3 = J(l, T)$ $Y_4 = J(c, p)$ $Z_4 = J(n, v)$ $Y_5 = J(a, p)$ $Z_5 = J(l, v)$ $Y_6 = J(c, T)$ $Z_6 = J(n, T)$	$a = (\partial v/\partial p)_T$ $b = (\partial v/\partial T)_p = -(\partial S/\partial p)_T$ $c = (\partial S/\partial T)_p$ $l = 1$ $n = b^2 + ac = \partial(v, S)/\partial(p, T)$	$a = 1$ $b = -(\partial p/\partial T)_v = -(\partial S/\partial v)_T$ $c = nl - b^2 = \partial(p, S)/\partial(v, T)$ $l = (\partial p/\partial v)_T$ $n = (\partial S/\partial T)_v$	$a = nl - b^2 = \partial(v, T)/\partial(p, S)$ $b = (\partial T/\partial p)_S = (\partial v/\partial S)_p$ $c = 1$ $l = (\partial T/\partial S)_p$ $n = (\partial v/\partial p)_S$	$a = (\partial T/\partial S)_v$ $b = (\partial T/\partial v)_S = -(\partial p/\partial S)_v$ $c = (\partial p/\partial v)_S$ $l = b^2 + ac = \partial(p, T)/\partial(v, S)$ $n = 1$	$a = -(\partial T/\partial p)_v$ $b = 1$ $c = (\partial S/\partial v)_p$ $l = (\partial T/\partial v)_p$ $n = (1 + ac)/l = -(\partial S/\partial p)_v$	$a = -(\partial v/\partial S)_T$ $b = 1$ $c = (\partial p/\partial T)_S$ $l = -(\partial p/\partial S)_T$ $n = (1 + ac)/l = (\partial v/\partial T)_S$
$C_p = Tc/l$ $C_v = Tn/a$		$Y_1 = (\partial^2 v/\partial p^2)_T$ $Y_2 = -(\partial^2 S/\partial p^2)_T = \partial^2 v/\partial p\,.\,\partial T$ $Y_3 = -(\partial^2 v/\partial T^2)_p = \partial^2 S/\partial p\,.\,\partial T$ $Y_4 = -(\partial^2 S/\partial T^2)_p$	$Z_1 = (\partial^2 p/\partial T^2)_v = \partial^2 S/\partial v\,.\,\partial T$ $Z_2 = -(\partial^2 S/\partial v^2)_T = -\partial^2 p/\partial v\,.\,\partial T$ $Z_3 = (\partial^2 p/\partial v^2)_T$ $Z_4 = -(\partial^2 S/\partial T^2)_v$	$R_1 = (\partial^2 T/\partial p^2)_S = \partial^2 v/\partial p.\partial S$ $R_2 = -(\partial^2 T/\partial S^2)_p$ $R_3 = (\partial^2 v/\partial p^2)_S$ $R_4 = -(\partial^2 v/\partial S^2)_p$ $= -\partial^2 T/\partial p\,.\,\partial S$	$S_1 = -(\partial^2 T/\partial S^2)_v$ $S_2 = (\partial^2 p/\partial v^2)_S$ $S_3 = (\partial^2 p/\partial S^2)_v = -\partial^2 T/\partial v\,.\,\partial S$ $S_4 = (\partial^2 T/\partial v^2)_S = -\partial^2 p/\partial v\,.\,\partial S$	$M_1 = \partial^2 T/\partial p\,.\,\partial v$ $M_2 = -(\partial^2 T/\partial p^2)_v$ $M_3 = -(\partial^2 S/\partial v^2)_p$ $M_4 = \partial^2 S/\partial p\,.\,\partial v$	$N_1 = (\partial^2 v/\partial S^2)_T$ $N_2 = -\partial^2 v/\partial T\,.\,\partial S$ $N_3 = -\partial^2 p/\partial T\,.\,\partial S$ $N_4 = (\partial^2 p/\partial T^2)_S$
$R_1 = J(b, S)$ $S_1 = J(a, v)$ $R_2 = J(l, p)$ $S_2 = J(c, S)$ $R_3 = J(n, S)$ $S_3 = J(b, v)$ $R_4 = J(b, p)$ $S_4 = J(b, S)$ $R_5 = J(l, S)$ $S_5 = J(a, S)$ $R_6 = J(n, p)$ $S_6 = J(c, v)$	$M_1 = J(a, p)$ $N_1 = J(a, T)$ $M_2 = J(a, v)$ $N_2 = J(a, S)$ $M_3 = J(c, p)$ $N_3 = J(c, T)$ $M_4 = J(c, v)$ $N_4 = J(c, S)$ $M_5 = J(l, v)$ $N_5 = J(l, S)$ $M_6 = J(n, p)$ $N_6 = J(n, T)$	$Y_5 = -Y_2$ $Y_6 = Y_3$	$Z_5 = Z_2$ $Z_6 = Z_1$	$R_5 = -R_4$ $R_6 = -R_1$	$S_5 = -S_3$ $S_6 = S_4$	$M_5 = M_1$ $M_6 = M_4$	$N_5 = N_2$ $N_6 = N_3$
		$C_p = Tc$ $C_v = Tn/a = T(b^2 + ac)/a$	$C_p = Tc/l = T(nl - b^2)/l$ $C_v = Tn$	$C_p = T/l$ $C_v = Tn/a = Tn/(nl - b^2)$	$C_p = Tc/l = Tc(b^2 + ac)$ $C_v = T/a$	$C_p = Tc/l$ $C_v = Tn/a = T(1 + ac)/al$	$C_p = Tc/l$ $C_v = Tn/a = T(1 + ac)/al$

* S_1, S_2, S_3, S_4, S_5, and S_6 must not be confused with S, the entropy.

Table IV—Table of Alternative Expressions for $J[J(x, y), z]$. For use in Transforming Partial Second Derivatives

(Each row consists of equivalent expressions for the same α and β only.)

	In terms of Y's	In terms of Z's	In terms of R's	In terms of S's*	In terms of M's	In terms of N's	
$J(a, p)$	Y_5	$Z_5 - Z_2$	$J(l, v) - J(b, T)$	$(cS_1 - bS_5)/n$	M_1	$(cN_1 - lN_2)/b$	$J[J(v, T), p]$
$J(a, v)$	$(bY_1 + aY_5)/l$	$[bJ(a, S) + nJ(a, p)]/c$	$[nJ(a, p) + bJ(a, S)]/c$	S_1	M_2	$(nN_1 - aN_2)/b$	$J[J(v, T), v]$
$J(a, T)$	Y_1	$[lJ(a, S) + bJ(a, p)]/c$	$[bJ(a, p) + lJ(a, S)]/c$	$(bS_1 + aS_5)/n$	$(-aM_1 + lM_2)/b$	N_1	$J[J(v, T), T]$
$J(a, S)$	$(cY_1 - bY_5)/l$	$Z_6 - Z_1$	$J(n, T) - J(b, v)$	S_5	$(-nM_1 + cM_2)/b$	N_2	$J[J(v, T), S]$
$J(b, p)$	Y_3	$(lZ_1 - bZ_2)/a$	R_4	$(cS_3 - bS_4)/n$	$[cJ(b, T) - lJ(b, S)]/b$	$N_3 - N_5$	$J[J(p, v), p] = J[J(T, S), p]$
$J(b, v)$	$(bY_2 + aY_3)/l$	Z_1	$(nR_4 + bR_1)/c$	S_3	$[nJ(b, T) - aJ(b, S)]/b$	$N_6 - N_2$	$J[J(p, v), v] = J[J(T, S), v]$
$J(b, T)$	Y_2	Z_2	$(bR_4 + lR_1)/c$	$(bS_3 + aS_4)/n$	$M_5 - M_1$	$[-aJ(b, p) + lJ(b, v)]/b$	$J[J(p, v), T] = J[J(T, S), T]$
$J(b, S)$	$(cY_2 - bY_3)/l$	$(-bZ_1 + nZ_2)/a$	R_1	S_4	$M_4 - M_6$	$[-nJ(b, p) + cJ(b, v)]/b$	$J[J(p, v), S] = J[J(T, S), S]$
$J(c, p)$	Y_4	$[lJ(c, v) - bJ(c, T)]/a$	$[lJ(c, v) - bJ(c, T)]/a$	$(cS_6 - bS_2)/n$	M_3	$(cN_3 - lN_4)/b$	$J[J(p, S), p]$
$J(c, v)$	$(bY_6 + aY_4)/l$	$(J(n, p) + J(b, S)$	$R_3 + R_6$	S_6	M_4	$(nN_3 - aN_4)/b$	$J[J(p, S), v]$
$J(c, T)$	Y_6	$J(l, S) + J(b, p)$	$R_4 + R_5$	$(bS_6 + aS_2)/n$	$(-aM_3 + lM_4)/b$	N_3	$J[J(p, S), T]$
$J(c, S)$	$(cY_6 - bY_4)/l$	$[nJ(c, T) - bJ(c, v)]/a$	$[nJ(c, T) - bJ(c, v)]/a$	S_2	$(-nM_3 + cM_4)/b$	N_4	$J[J(p, S), S]$
$J(l, p)$	$[cJ(l, v) - bJ(l, S)]/n$	$(lZ_2 - bZ_3)/a$	R_2	$[cJ(l, v) - bJ(l, S)]/n$	$[cJ(l, v) - bJ(l, S)]/n$	$[cJ(l, v) - bJ(l, S)]/n$	$J[J(p, T), p]$
$J(l, v)$	$Y_2 + Y_5$	Z_5	$(nR_2 + bR_5)/c$	$J(b, T) + J(a, p)$	M_5	$J(b, T) + J(a, p)$	$J[J(p, T), v]$
$J(l, T)$	$[bJ(l, v) + aJ(l, S)]/n$	Z_3	$(bR_2 + lR_5)/c$	$[bJ(l, v) + aJ(l, S)]/n$	$[bJ(l, v) + aJ(l, S)]/n$	$[bJ(l, v) + aJ(l, S)]/n$	$J[J(p, T), T]$
$J(l, S)$	$Y_6 - Y_3$	$(nZ_2 - bZ_5)/a$	R_5	$J(c, T) - J(b, p)$	$J(c, T) - J(b, p)$	N_5	$J[J(p, T), S]$
$J(n, p)$	$J(c, v) - J(b, S)$	$(lZ_4 - bZ_6)/a$	R_6	$S_6 - S_4$	M_6	$J(c, v) - J(b, S)$	$J[J(v, S), p]$
$J(n, v)$	$[bJ(n, T) + aJ(n, p)]/l$	Z_4	$(nR_6 + bR_3)/c$	$[bJ(n, T) + aJ(n, p)]/l$	$[aJ(n, p) + bJ(n, T)]/l$	$[aJ(n, p) + bJ(n, T)]/l$	$J[J(v, S), v]$
$J(n, T)$	$J(a, S) + J(b, v)$	Z_6	$(bR_6 + lR_3)/c$	$S_3 + S_5$	$J(a, S) + J(b, v)$	N_6	$J[J(v, S), T]$
$J((n, S)$	$[cJ(n, T) - bJ(n, p)]/l$	$(nZ_6 - bZ_4)/a$	R_3	$[cJ(n, T) - bJ(n, p)]/l$	$[-bJ(n, p) + cJ(n, T)]/l$	$[-bJ(n, p) + cJ(n, T)]/l$	$J[J(v, S), S]$

If $x = a, b, c, l$ or n (or any other function of α and β), we have,

$$J(x, E) = [(Tc - pb)\,J(x, T) - (Tb + pa)\,J(x, p)]/l$$
$$J(x, I) = [(Tc\,J(x, T) + (vl - Tb)\,J(x, p)]/l$$
$$J(x, F) = -[(Sl + pb)\,J(x, T) + paJ(x, p)]/l$$

$$J(x, G) = -SJ(x, T) + vJ(x, p)$$
$$J(x, Q) = [Tc\,J(x, T) - Tb\,J(x, p)]/l$$
$$J(x, W) = [pbJ(x, T) + paJ(x, p)]/l$$

* Note that S_1, S_2, S_3, S_4, S_5, and S_6, used in this column, must not be confused with S, the entropy.