Condensed Collections of Thermodynamic Formulas for One-Component and Binary Systems of Unit and Variable Mass

George Tunell

Publication No. 408B

Carnegie Institution of Washington

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Preface

A collection of thermodynamic formulas for a system of one component and of fixed mass was published by P.W. Bridgman in 1914 in the Physical Revue and an emended and expanded version by him was published by the Harvard University Press in 1925 under the title *A Condensed Collection of Thermodynamic Formulas.* In 1935 A.N. Shaw presented a table of Jacobians for a system of one component and of fixed mass and explained its use in the derivation of thermodynamic relations for such a system in an article entitled "The Derivation of Thermodynamical Relations for a Simple System" published in the Philosophical Transactions of the Royal Society of London. A collection of thermodynamic formulas for multi-component systems of variable total mass by R.W. Goranson appeared in 1930 as Carnegie Institution of Washington Publication No. 408 entitled *Thermodynamical Relations in Multi-Component Systems.* Unfortunately, Goranson had accepted the erroneous assumption made by Sir Joseph Larmor in his obituary notice of Josiah Willard Gibbs (Proceedings of the Royal Society of London, Vol. 75, pp. 280-296, 1905) that the differential of the heat received by an open system is equal to the absolute thermodynamic temperature times the differential of the entropy, $dQ = TdS$. In consequence of this error Goranson's basic equations for the energy and the entropy of a multi-component system are incorrect. In 1933 L.J. Gillespie and J.R. Coe, Jr., in an article published in volume three of the Journal of Chemical Physics showed that in the case of an open system, "the complete variation of the entropy, for simultaneous reversible transfers of heat and mass, is

$$dS = \frac{dq}{T} + \Sigma s_1\, dm_1 \text{."}$$

In this equation *dS* denotes the increase in the entropy of the open system, *dq* the amount of heat received by the open system, *T* the absolute thermodynamic temperature, s_x the entropy of unit mass of kind 1 added to the open system, and dm_1 the mass of kind 1 added to the open system. This equation is inconsistent with Goranson's basic equations for the energy and the entropy of a multi-component system and is also inconsistent with very many expressions in his tables for first and second derivatives in the case of a multi-component system. Gibbs showed in his memoir entitled "On the Equilibrium of Heterogeneous Substances" (Trans. Conn. Acad. of Arts and Sciences, Vol. 3, pp. 108-248 and 343-524, 1874-78) that it is possible to determine the energy and the entropy of a multi-component system by measurements of heat quantities and work quantities in closed systems. On this basis, the present author made a detailed analysis of the measurements necessary to obtain complete thermodynamic information for a binary system of one phase over a given range of temperature, pressure, and composition without involving definitions of heat or work in the case of open systems, which was published in a book entitled *Relations between Intensive Thermodynamic Quantities and Their First Derivatives in a Binary System of One Phase* (W.H. Freeman and Company, 1960.) In this book the present author also presented a table by means of which any desired relation between the absolute thermodynamic temperature *T,* the pressure p, the mass fraction of one component m_1, the specific volume *V,* the specific energy *U,* and the specific entropy *S,* and their first derivatives for a binary system of one phase can be derived from the experimentally determined relations by the use of functional determinants (Jacobians).

In the present work, tables of Jacobians are given for one-component systems of unit mass and of variable mass and for binary systems of unit mass and of variable total mass by means of which relations can be obtained between the thermodynamic quantities and their first derivatives. An explanation of the experimental measurements necessary to obtain complete thermodynamic information in each of these cases is also provided. The table of Jacobians for the case of a one-component system of unit mass is included for comparison with the other tables of Jacobians, because the Jacobians in the tables in the other three cases reduce essentially to those in the table for the case of the one-component system of unit mass when the masses are held constant. The Jacobians in the table in the present text for the case of a one-component system of unit mass are the same as the expressions in Bridgman's tables for this case. The Jacobians in the tables in the present text for the case of a binary system of unit mass differ slightly in form from those in Table 1 of this author's book entitled *Relations between Intensive Thermodynamic Quantities and Their First Derivatives in a Binary System of One Phase.* It has been found that by elimination of the special symbols ξ_1 and σ_1 for $\left(\frac{\partial U}{\partial m_1}\right)_{T,p}$ and $\left(\frac{\partial \breve{S}}{\partial m_1}\right)_{T,p}$ and adherence to the symbols $\left(\frac{\partial \breve{U}}{\partial m_1}\right)_{T,p}$ and $\left(\frac{\partial S}{\partial m_1}\right)_{T,p}$ a simpler and more perspicuous arrangement of the terms in the Jacobians results in this case. The Jacobians in the new tables in the present text for the case of a binary system of variable total mass differ very much from the expressions in the tables in Carnegie Institution of Washington Publication No. 408 by R.W. Goranson. Very many of the expressions in Goranson's tables are incorrect on account of his erroneous assumption that $dQ = TdS$ in the case of open systems when there is simultaneous reversible transfer of both heat and mass. Furthermore, Goranson's expressions in his tables for first derivatives in such cases are not formulated in terms of the minimum number of derivatives chosen as fundamental as he himself recognized.

As might be expected there is a considerable parallelism between the Jacobians in the tables in the present text for a one-component system of one phase and of variable mass and those in the tables in the present text for a binary system of one phase and of unit mass. There is also a partial parallelism between the Jacobians in the tables in the present text for the two cases just mentioned and those in the present text for the case of a binary system of one phase and of variable total mass. Thus for example in the case of a one-component system of one phase and of variable mass we have

$$\frac{\partial(S, V, U)}{\partial(T, p, M)} = M^2\left\{\left[\breve{U} + p\breve{V} - T\breve{S}\right]\left[\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]\right\},$$

where S denotes the total entropy, V the total volume, U the total energy, T the absolute thermodynamic temperature, p the pressure, M the mass, $\breve{S}$ the specific entropy, $\breve{V}$ the specific volume, $\breve{U}$ the specific energy, and $\breve{c}_p$ the heat capacity at constant pressure per unit of mass. For comparison in the case of a binary system of one phase and of unit mass we have

$$\frac{\partial(\breve{S}, \breve{V}, \breve{U})}{\partial(T, p, \breve{m}_1)} = \left[\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]$$

$$\cdot\left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right],$$

Correspondence of Tables of Jacobians

Part I Table 1-1	Part II Tables II-l to 11-15	Part III Tables III-l to 111-15	Part IV Tables IV-1 to IV-35
	1	1	1 & 2
1	2	2	6
	3	3	7 & 10
	4	4	8 & 11
	5	5	9 & 12
1	6	6	16
	7	7	17 & 20
	8	8	18 & 21
	9	9	19 & 22
1	10	10	26
1	11	11	27
1	12	12	28
	13	13	29 & 32
	14	14	30 & 33
	15	15	31 & 34
			3
			4
			5
			13
			14
			15
			23
			24
			25
			35

where $\breve{m}_1$ denotes the mass fraction of component 1, which is equal to m_1, the mass of component 1, divided by the sum of m_1 and m_2, m_2 denoting the mass of component 2.

Furthermore in the case of a binary system of one phase and of variable total mass we have

$$\frac{\partial(S, m_1, V, U)}{\partial(T, p, m_1, m_2)}$$

$$= -(m_1 + m_2)^2\left\{\left[(\breve{U} + p\breve{V} - T\breve{S}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p}\right)\right]\right.$$

$$\left.\cdot\left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\,\breve{m}_1} + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right]\right\}.$$

Also we have

$$\frac{\partial(S, m_2, V, U)}{\partial(T, p, m_1, m_2)}$$

$$= (m_1 + m_2)^2\left\{\left[(\breve{U} + p\breve{V} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p}\right)\right]\right.$$

$$\left.\cdot\left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\,\breve{m}_1} + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right]\right\}.$$

The last factor in each of these four Jacobians is the same. In the case of the next to the last factor in each of these Jacobians there is some parallelism; thus the next to the last factor in the case of the Jacobian $\frac{\partial(S, V, U)}{\partial(T, p, M)}$ is $(\breve{U} + p\breve{V} - T\breve{S})$ which is equal to the specific Gibbs function $\breve{G}$ or $\frac{G}{M}$. The next to the last factor in the case of the

Jacobian $\dfrac{\partial(\breve{S}, \breve{V}, \breve{U})}{\partial(T, p, \breve{m}_1)}$ is $\left\{\left(\dfrac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\dfrac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\dfrac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right\}$

which is equal to $\left(\dfrac{\partial \breve{G}}{\partial \breve{m}_1}\right)_{T, p}$. Finally the next to the last factor in the case of the Jacobian $\dfrac{\partial(S, m_1, V, U)}{\partial(T, p, m_1, m_2)}$ is

$$\left[(\breve{U} + p\breve{V} - T\breve{S}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right)\right]$$

which is equal to $\left(\dfrac{\partial G}{\partial m_2}\right)_{T, p, m_1}$ and the next to the last factor in the case of the Jacobian $\dfrac{\partial(S, m_2, V, U)}{\partial(T, p, m_1, m_2)}$ is

$$\left[(\breve{U} + p\breve{V} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right)\right]$$

which is equal to $\left(\dfrac{\partial G}{\partial m_1}\right)_{T, p, m_2}$. It is to be noted that in all of these four Jacobians a simplification would result if use were made of the Gibbs function G and its derivatives; however, in the tables this would introduce more first derivatives than the minimum number of fundamental derivatives in terms of which all first derivatives are expressible. If it is merely desired to calculate a particular derivative as the quotient of two Jacobians, the introduction of the Gibbs function G (likewise the introduction of the enthalpy, $H \equiv U + pV$, and the Helmholtz function, $A \equiv U - TS$) in the expressions for the Jacobians would cause no difficulty. On the other hand if it is desired to obtain a relation among certain derivatives by expressing them in terms of the minimum number of fundamental derivatives and then eliminating the fundamental derivatives from the equations, the introduction of the Gibbs function *G* (or the enthalpy *H* or the Helmholtz function *A)* in the expressions for the Jacobians would defeat the purpose.

The basic theorem on Jacobians that is needed in the calculation of derivatives of point functions with respect to a new set of independent variables in terms of derivatives with respect to an original set of independent variables was stated by Bryan (in *Encyklopädie der matematischen Wissenschaften,* B.G. Teubner, Leipzig, Bd. V, Teil 1, S. 113, 1903), and is mentioned (without proof) in a number of textbooks on the calculus. Proofs of this theorem in cases of functions of two independent variables and functions of three independent variables are given in Appendix B to Part I and Appendix C to Part II of the present work. In the case of transformations of line integrals that depend upon the path from one coordinate system to another coordinate system, the Jacobian theorem does not apply. To cover this case a new theorem is needed. The new theorem developed by the present author for the expression of the derivatives of a line integral that depends upon the path along lines parallel to the coordinate axes in one plane or space in terms of the derivatives of the line integral along lines parallel to the coordinate axes in other planes or spaces is stated and proved in Appendix B to Part I and Appendix C to Part II of the present work (this theorem is expressed by equations (I-B-36) and (I-B-37) in Appendix B to Part I and equations (II-C-63), (II-C-64), and (II-C-65) in Appendix C to Part II). It is a pleasure to acknowledge my indebtedness to Professor C.J.A. Halberg, Jr., and Professor V.A. Kramer, both of the Department of Mathematics of the University of California at Riverside, who have kindly examined my proof of this theorem carefully and in detail and who have confirmed its correctness. I wish also to express my gratitude to Mrs. Sheila Marshall for carefully and skillfully typing the manuscript of this book in form camera-ready for reproduction by offset photolithography and to Mr. David Crouch for making the drawings for Figures II-l, II-A-1, II-A-2, and IV-A-1.

George Tunell

Santa Barbara, California
August 1984

Contents

Part I

Relations between thermodynamic quantities and their first derivatives in a one-component system of one phase and of unit mass

Introduction

In consequence of the first and second laws of thermodynamics and the equation of state of a one-component system of one phase and of unit mass there are very numerous relations between the thermodynamic quantities of such a system and their derivatives. Bridgman[1] devised a table of functions by means of which any first derivative of a thermodynamic quantity of such a system can be evaluated in terms of the three first derivatives, $\left(\frac{\partial \breve{V}}{\partial p}\right)_T$, $\left(\frac{\partial \breve{V}}{\partial T}\right)_p$, and $\breve{C}_p$, together with the absolute thermodynamic temperature and the pressure, as a quotient of two of the tabulated functions. The equation among any four first derivatives can then be obtained by elimination of the three derivatives, $\left(\frac{\partial \breve{V}}{\partial p}\right)_T$, $\left(\frac{\partial \breve{V}}{\partial T}\right)_p$, and $\breve{C}_p$, from the four equations expressing the four first derivatives in terms of the three derivatives, $\left(\frac{\partial \breve{V}}{\partial p}\right)_T$, $\left(\frac{\partial \breve{V}}{\partial T}\right)_p$, and $\breve{C}_p$.

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[1] Bridgman, P.W., Phys. Rev., (2), 3, 273-281, 1914, also *A Condensed Collection of Thermodynamic Formulas,* Harvard University Press, Cambridge, 1925.

Bridgman's table has been found very useful and has become well known. The functions in Bridgman's table can be derived by a simpler method, however. The theorem upon which this method is based had been stated by Bryan,[2] but a proof of this theorem is not included in the article by Bryan. In the following pages the functions tabulated by Bridgman are derived by the method of Jacobians explained by Bryan and the Jacobian theorem is proved.

Equation of state of a one-component system of one phase

The principal properties of a one-component system of one phase and of unit mass that are considered in thermodynamics are the absolute thermodynamic temperature T, the pressure p, the specific volume 7, the specific energy *U,* and the specific entropy 5. It has been established experimentally that the temperature, the pressure, and the specific volume are related by an equation of state

$$*(p, \breve{V}, T) = 0. \qquad (1\text{-}1)$$

Even if an algebraic equation with numerical coefficients cannot be found that will reproduce the experimental data for a particular one-component system within the accuracy of the measurements over the entire range of the measurements, the equation of state can still be represented graphically with such accuracy, and numerical values can be scaled from the graphs.[3]

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[2] Bryan, G.H., in *Encyklopädie der matematischen Missenschaften,* B.G. Teubner, Leipzig, Bd, V, Teil 1, S. 113, 1903.

[3] **Deming, W.E.,** and L.E. Shupe, Phys. Rev., (2), 37, 638-654, 1931; York, Robert, Jr., Industrial and Engineering Chemistry, **32, 54-56,** 1940.

Work done and heat received by the system

One may plot the values of the temperature *T* and the pressure p of the system in a series of states through which the system passes, laying off the values of *T* along one coordinate-axis and the values of p along the other coordinate-axis. The points representing the series of states then form a curve, which, following Gibbs[4] one may call the path of the system. As Gibbs further pointed out, the conception of a path must include the idea of direction, to express the order in which the system passes through the series of states. With every such change of state there is connected a certain amount of work, *W,* done by the system, and a certain amount of heat, *Q,* received by the system, which Gibbs[5] and Maxwell[6] called the work and the heat of the path. Since the temperature and pressure are supposed uniform throughout the system in any one state, all states are equilibrium states, and the processes discussed are reversible processes.

The work done by this system on the surroundings is expressed mathematically by the equation

$$W = \int_{V_0}^{V} p\,dV. \tag{1-2}$$

[4] Gibbs, J. Willard, Trans. Conn. Acad. of Arts and Sciences, 2, 311, 1871-73, or *Collected Works,* Longmans, Green and Co., New York, 1928, Vol. 1, p. 3.

[5] Gibbs, J. Willard, Trans. Conn. Acad. of Arts and Sciences, 2, 311, 1871-73, or *Collected Works,* Longmans, Green and Co., New York, 1928, Vol. 1, p. 3.

[6] Maxwell, J. Clerk, *Theory of Heat,* 10th Ed., Longmans, Green and Company, London, 1891, p. 186.

The value of this integral depends upon the particular path in the (p, V)-plane, and when the path is determined, for example, by the relation

$$p = f(V), \tag{1-3}$$

the value of the integral can be calculated.

If the path is plotted in the (T, p)-plane the work done by the system, W, may be obtained by transformation of the integral in equation (1-2)

$$W = \int_{T_0,\,p_0}^{T,\,p} \left\{ p\left(\frac{\partial V}{\partial T}\right)_p dT + p\left(\frac{\partial V}{\partial p}\right)_T dp \right\}, \tag{1-4}$$

and the path may be determined in this case by the relation

$$p = \varphi(T). \tag{1-5}$$

Similarly the heat, Q, received by the system,

$$Q = \int_{T_0,\,P_0}^{T,\,P} \left\{ c_p\, dT + l_p\, dp \right\}, \tag{1-6}$$

may be calculated provided the heat capacity at constant pressure per unit of mass, c_p, and the latent heat of change of pressure at constant temperature per unit of mass, l_p, are known functions of T and p and the path is determined by equation (1-5). The integrals in equations (1-4) and (1-6) are line integrals[7] that depend upon the particular choice of the path.

---

[7] For the definition of a line integral, see W.F. Osgood, *Advanced Calculus*, The Macraillan Company, New York, 1925, pp. 220, 221, or R. Courant, *Differential and Integral Calculus*, translated by J.E. McShane, Blackie & Son, Ltd,, London, 1944, Vol. 2, pp. 344, 345.

First and second laws of thermodynamics applied to a one-conponent system of one phase and of unit mass

The first law of thermodynamics for a one-component system of one phase and of unit mass traversing a closed path or cycle is the experimentally established relation

$${dQ - dW} = 0.^8 \qquad (1\text{-}7)$$

Replacing *<PdQ* and *$dW* by their values from equations (1-4) and (1-6) in order that the integral may be expressed in terms of the coordinates of the plane in which the path is plotted, one has

/{[*" -p(if)p y • [rp -p(f)T]}dp = 0. (I-8)

---

[8] Blondlot, R., *Introduction a l'Étude de la Thermodynamique*, Gauthier-Villars et Fils, Paris, 1888, p. 66; Bryan, G.H., op. cit., p. 83; Poincare, H., *Thermodynamique*, Second Edition, Edited by J. Blondin, Gauthier-Villars et Cie, Paris, 1923, p. 69; Keenan, J.H., *Thermodynamics,* John Wiley & Sons, Inc., New York, 1941, p. 10; Allis, W.P., and M.A. Herlin, *Thermodynamics and Statistical Mechanics,* McGraw-Hill Book Co., Inc., New York, 1952, p. 67; Schottky, W., H. Ulich, and C. Wagner, *Thermodynamik, die Lehre von den Kreisprozessen, den physikalischen und chemischen Veränderungen und Gleichgewichten,* Julius Springer, Berlin, 1929, pp. 14-15.

Lord Kelvin in his paper entitled "*On* the dynamical theory of heat, with numerical results deduced from Mr. Joule's equivalent of a thermal unit, and M. Regnault's observations on steam" (Trans. Roy. Soc* Edinburgh, 20, 261-288, 1851) made the following statement: "Let us suppose a mass of any substance, occupying a volume v, under a pressure p uniform in all directions, and at a temperature t, to expand in volume to v + dv, and to rise in temperature to t + dt. The quantity of work which it will produce will be

$$pdv;$$

and the quantity of heat which must be added to it to make its temperature rise during the expansion to t + dt may be denoted by

$$Mdv + Ndt,$$

From equation (1-8) it follows that the integral

$$\int_{T_0, p_0}^{T, p} \left\{ \left[\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_p \right] dT + \left[\breve{l}_p - p\left(\frac{\partial \breve{V}}{\partial p}\right)_T \right] dp \right\}$$

is independent of the path and defines a function of the

The mechanical equivalent of this is

JiMdv + Ndt),

if J denote the mechanical equivalent of a unit of heat. Hence the mechanical measure of the total external effect produced in the circumstances is

(p - *JM)dv - JNdt.*

The total external effect, after any finite amount of expansion, accompanied by any continuous change of temperature, has taken place, will consequently be, in mechanical terms,

/{(p - *JM)dv - JNdt} ;*

where we must suppose *t* to vary with v, so as to be the actual temperature of the medium at each instant, and the integration with reference to *v* must be performed between limits corresponding to the initial and final volumes. Now if, at any subsequent time, the volume and temperature of the medium become what they were at the beginning, however arbitrarily they may have been made to vary in the period, the total external effect must, according to Prop. I., amount to nothing; and hence

(p - *JM)dv - JNdt*

must be the differential of a function of two independent variables, or we must have

$$\frac{dip - JM)}{dt} = \frac{d(-JN)}{dv} \qquad \text{M.} \; (1),$$

this being merely the analytical expression of the condition, that the preceding integral may vanish in every case in which the initial and final values of v and *t* are the same, respectively,ⁿ And elsewhere in the same paper Lord Kelvin wrote: "Prop, I. (Joule).-When equal quantities of mechanical effect are produced by any means whatever, from purely thermal sources, or lost in purely thermal effects, equal quantities of heat are put out of existence or are generated/[1]

coordinates; this function, to which the name energy is given and which is here denoted by the letter U, is thus a function of the state of the system

$\breve{U}(T, p) - \breve{U}(T_0, p_0) =$

`Kb - '$)>• & - 4\] 4 •    «H»`

T_0, p_0

The second law of thermodynamics for a one-component system of one phase and of unit mass traversing a closed reversible path or cycle is the experimentally established relation

$$\oint f- = 0 ,^{9} \qquad (1\text{-}10)$$

where T is the temperature on the absolute thermodynamic scale. Expressing this integral in terms of the coordinates of the plane in which the path is plotted, one has

$$\oint \left\{ \frac{\breve{c}_p}{T} \, dT + \frac{\breve{l}_p}{T} \, dp \right\} = 0 . \qquad (\text{I-11})$$

---

[9] Clausius, R., Die *mechanische Wärmetheorie*, Dritte aufl., Bd. I, Friedrich Vieweg und Sohn, Braunschweig, 1887, S. 93; Blondlot, R., op. **cit.**, p. 66; **Van't** Hoff, J.H., *Physical Chemistry in the Service of the Sciences*, English Version by A. Smith, University of Chicago Press, Chicago, 1903, pp. 21-22; Schottky, W., H. Ulich, and C. Wagner, op. cit., p. 17; Gibbs, J. Willard, Proceedings of the American Academy of Arts and Sciences, new series, 16, 460, 1889, or *Collected Works,* Vol. 2, Longmans, Green and Company, New York, 1928, p. 263.

From equation (1-11) it follows that the integral

$$\int_{T_o,\, p_0}^{T,\, p} \left\{ \frac{\breve{c}_p}{T} dT + \frac{\breve{l}_p}{T} dp \right\}$$

is independent of the path and defines a function of the coordinates; this function, to which the name entropy is given and which is here denoted by the letter $\breve{S}$, is thus a function of the state of the system

$$\breve{S}(T,p) - \breve{S}(T_o,p_o) = \int_{T_o,\, p_o}^{T,\, p} \left\{ \frac{\breve{c}_p}{T} dT + \frac{\breve{l}_p}{T} dp \right\} . \qquad \text{(I-12)}$$

From equation (1-9) it follows directly[10] that

$$\left(\frac{\partial \breve{U}}{\partial T}\right)_p = \breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_p \qquad \text{(I-13)}$$

and

$$\left(\frac{\partial \breve{U}}{\partial p}\right)_T = \breve{l}_p - p\left(\frac{\partial \breve{V}}{\partial p}\right)_T . \qquad \text{(I-14)}$$

From equation (1-12) it follows likewise that

$$\left(\frac{\partial \breve{S}}{\partial T}\right)_p = \frac{\breve{c}_p}{T} \qquad \text{(I-15)}$$

and

$$\left(\frac{\partial \breve{S}}{\partial p}\right)_T = \frac{\breve{l}_p}{T} . \qquad \text{(I-16)}$$

---

[10] For the proof of this theorem, see W.F. Osgood, op. cit., pp. 229-230, or R. Courant - J.E. McShane, op. cit., Vol. 1, pp. 352-355.

A necessary and sufficient condition[11] for equation (1-9) to be true is

$$\left\{\frac{\partial\left[\breve{l}_p - p\left(\frac{\partial \breve{v}}{\partial p}\right)_T\right]}{\partial T}\right\}_p = \left\{\frac{\partial\left[\breve{c}_p - p\left(\frac{\partial \breve{v}}{\partial T}\right)_p\right]}{\partial p}\right\}_T . \quad ^{12} \tag{1-17}$$

Likewise a necessary and sufficient condition for equation (1-12) to be true is

$$\left\{\frac{\partial \frac{\breve{l}_p}{T}}{\partial T}\right\}_p = \left\{\frac{\partial \frac{\breve{c}_p}{T}}{\partial p}\right\}_T . \quad ^{13} \tag{1-18}$$

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[11] For the proof of this theorem, see W.F. Osgood, op. cit., pp. 228-230, or R. Courant - J.E. McShane, op. cit., Vol. 1, pp. 352-355.

[12] Lord Kelvin wrote the analogous equation with t and v as the independent variables as an analytical expression of the "first fundamental proposition" or first lav; of thermodynamics. His statement follows: "Observing that J is an absolute constant, we may put the result into the form

$$\frac{dp}{dt} = J \frac{dM}{dt} - \frac{dN}{dv} \; .$$

This equation expresses, in a perfectly comprehensive manner, the application of the first fundamental proposition to the thermal and mechanical circumstances of any substance whatever, under uniform pressure in all directions, when subjected to any possible variations of temperature, volume, and pressure." (Trans. Roy. Soc. Edinburgh, 20, 270, 1851.) Clausius also stated that an analogous equation, his equation (5), forms an analytical expression of the first law for reversible changes in a system the state of which is determined by two independent variables. *(Abhandlungen iiher die mechanische Warmetheorie** Zweite Abtheilung, Abhandlung IX, Friedrich Vieweg und Sohn, Braunschweig, 1867, p. 9.)

[13] Clausius stated that his equation (6), to which equation (1-18) of this text is analogous, constituted an analytical expression of the second law for reversible processes in a system the state of which is determined by two independent variables. *(Abhandlungen iiber die mechanische Warmetheoriei* Zweite Abtheilung, Abhandlung IX, Friedrich Vieweg und Sohn, Braunschweig, 1867, p* 9.)

Carrying out the indicated differentiations one obtains from equation (1-17) the relation

$$\left(\frac{\partial \breve{l}_p}{\partial T}\right)_p \quad \frac{\partial^2 \breve{V}}{\partial T \partial p} \quad \left(\frac{\partial \breve{c}_p}{\partial p}\right)_T \quad \frac{\partial^2 \breve{V}}{\partial p \partial T} \quad \left(\frac{\partial \breve{V}}{\partial T}\right)_p \tag{1-19}$$

and from equation (1-18) the relation

$$T \ldots \Big)_p \; T \ldots \; T \ldots \Big)_T \; . \tag{1-20}$$

Combining equations (1-19) and (1-20) one has

$$\breve{l}_p = - \ldots \Big)_p \; . \tag{1-21}$$

From equations (1-19) and (1-21) it also follows that

$$\left(\frac{\partial \breve{c}_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 \breve{V}}{\partial T^2}\right)_p \; . \tag{1-22}$$

All the first derivatives of the three quantities *V, U** and *S* expressed as functions of *T* and p can thus be calculated from equations (1-13), (1-14), (1-15), (1-16), and (1-21) if $\left(\frac{\partial V}{\ldots}\right)_p$, $\left(\frac{\partial V}{\ldots}\right)_T$ and c_p have been determined experimentally.

In order to be able to calculate all the properties of this system at any temperature and pressure, the volume must be determined experimentally as a function of the temperature and pressure; the first two derivatives $\left(\frac{\partial V}{\ldots}\right)$ and $\left(\frac{\partial V}{\ldots}\right)$ can then be calculated at any temperature and pressure within the range over which the volume has been determined. The third derivative, $\breve{c}_p$, need only be determined experimentally along some line not at constant temperature,[14] since $\left(\frac{\partial \breve{c}_p}{\partial p}\right)_T$ can be calculated from equation (1-22) if $\left(\frac{\partial V}{\partial T}\right)_p$ has been determined as a function of T and p.

Derivation of any desired relation between the intensive thermodynamic quantities, T, p, V, U, S, and their first derivatives for a one-component system of one phase from the experimentally determined relations by the use of functional determinants (Jacobians)

Equations (1-1), (1-9), and (1-12) can be solved for any three of the quantities, T, p, V, U, S as functions of the remaining two. The first partial derivative of any one of the quantities, T, p, V, U, S with respect to any second quantity when any third quantity is held constant can readily be obtained in terms of the three first derivatives $\left(\frac{\partial V}{\partial T}\right)_p$, $\left(\frac{\partial V}{\partial p}\right)_T$, and $\breve{c}_p$, together with the absolute thermodynamic temperature and the pressure, by application of the theorem stating that if $x' = \varphi(x, y)$, if $x = f(u, v)$, and if $y = \psi(u, v)$, then one has

[14] Bridgman, P.W., Phys, Rev., (2), 3, 274, 1914.

$$\left(\frac{\partial x'}{\partial x}\right)_y = \frac{\begin{vmatrix} \left(\frac{\partial x'}{\partial u}\right)_v & \left(\frac{\partial x'}{\partial v}\right)_u \\ \left(\frac{\partial y}{\partial u}\right)_v & \left(\frac{\partial y}{\partial v}\right)_u \end{vmatrix}}{\begin{vmatrix} \left(\frac{\partial x}{\partial u}\right)_v & \left(\frac{\partial x}{\partial v}\right)_u \\ \left(\frac{\partial y}{\partial u}\right)_v & \left(\frac{\partial y}{\partial v}\right)_u \end{vmatrix}} = \frac{\dfrac{\partial(x', y)}{\partial(u, v)}}{\dfrac{\partial(x, y)}{\partial(u, v)}} \qquad (1\text{-}23)$$ [15]

provided all the partial derivatives in the determinants are continuous and provided the determinant in the denominator is not equal to zero. The symbol $\frac{\partial(x', y)}{\partial(u, v)}$ here denotes the Jacobian[16] of the functions x' and y with respect to the variables u and v and the symbol $\frac{\partial(x, y)}{\partial(u, v)}$ denotes the Jacobian of the functions x and y with respect to the variables u and v. In Table 1-1 the value of the Jacobian is given for each pair of the variables, T, p, V, U, S, as x', y or x, y and

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[15] Bryan, G.H., op. cit., p. 113, equation (82); see also Osgood, W.F., op. cit,, p. 150, Exercise 31, Burington, R.S., and C.C. Torranee. *Higher Mathematics with Applications to Science and Engineering,* McGraw-Hill Book Co., Inc., New York and London, 1939, p. 138, Exercise 7, and Sherwood, T.K., and C.E. Reed, *Applied Mathematics in Chemical Engineering,* McGraw-Hill Book Co., Inc., New York and London, 1939, p. 174, equation (164). A proof of this theorem for the case of functions of two independent variables is given in Appendix B to Part I.

[16] For the definition of a Jacobian, see W.B. Fite, *Advanced Calculus,* The Macmillan Company, Hew York, 1938, pp. 308-309.

with T, p as u, v. There are 20 Jacobians in the table, but one has $\frac{\partial(x, y)}{\partial(u, v)} = - \frac{\partial(y, x)}{\partial(u, v)}$, because interchanging the rows of the determinant changes the sign of the determinant; hence it is only necessary to calculate the values of 10 of the determinants. The calculations of these ten determinants follow:

$$\frac{\partial(p, T)}{\partial(T, p)} = \begin{vmatrix} \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} \end{vmatrix} = -1 ; \qquad (1\text{-}24)$$

$$\frac{\partial(\breve{V}, T)}{\partial(T, p)} = \begin{vmatrix} \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} \end{vmatrix} = -\left(\frac{\partial \breve{V}}{\partial p}\right)_T ; \qquad (1\text{-}25)$$

$$\frac{\partial(\breve{E}, T)}{\partial(T, p)} = \begin{vmatrix} \frac{\partial \breve{E}}{\partial T} & \frac{\partial \breve{E}}{\partial p} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} \end{vmatrix} = T\left(\frac{\partial \breve{V}}{\partial T}\right)_p + p\left(\frac{\partial \breve{V}}{\partial p}\right)_T ; \qquad (I\text{-}26)$$

$$\frac{\partial(\breve{S}, T)}{\partial(T, p)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} \end{vmatrix} = \left(\frac{\partial \breve{V}}{\partial T}\right)_p ; \qquad (1\text{-}27)$$

$$\frac{\partial(\breve{V}, p)}{\partial(T, p)} = \begin{vmatrix} \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} \end{vmatrix} = \left(\frac{\partial \breve{V}}{\partial T}\right)_p ; \qquad (1\text{-}28)$$

$$\frac{\partial(\breve{U}, p)}{\partial(T, p)} = \begin{vmatrix} \frac{\partial \breve{U}}{\partial T} & \frac{\partial \breve{U}}{\partial p} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} \end{vmatrix} = \breve{C}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_p ; \tag{1-29}$$

$$\frac{\partial(\breve{S}, p)}{\partial(T, p)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} \end{vmatrix} = \frac{\breve{C}_p}{T} ; \tag{1-30}$$

$$\frac{\partial(\breve{U}, \breve{V})}{\partial(T, p)} = \begin{vmatrix} \frac{\partial \breve{U}}{\partial T} & \frac{\partial \breve{U}}{\partial p} \\ \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} \end{vmatrix} = T\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \breve{C}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_T ; \tag{1-31}$$

$$\frac{\partial(\breve{S}, \breve{V})}{\partial(T, p)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} \\ \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} \end{vmatrix} = \left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T ; \tag{1-32}$$

$$\frac{\partial(\breve{S}, \breve{U})}{\partial(T, p)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} \\ \frac{\partial \breve{U}}{\partial T} & \frac{\partial \breve{U}}{\partial p} \end{vmatrix} = -p\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 - \frac{p\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T . \tag{1-33}$$

In order to obtain the first partial derivative of any one of the five quantities T, p, $\breve{V}$, $\breve{U}$, $\breve{S}$ with respect to any second quantity of the five when any third quantity of the five is held constant, one has only to divide the value of the **Jacobian** in Table 1-1 in which the first letter in the first line is the quantity being differentiated and in which the second letter in the first line is the quantity held constant

Table 1-1
Jacobians of intensive functions for a one-component system of one phase

$$\frac{\partial(x', y)}{\partial(T, p)} \quad , \quad \frac{\partial(x, y)}{\partial(T, p)}$$

x \ y	T	p	$\tilde V$	$\tilde U$	$\tilde S$
T	~	1	$\left(\frac{\partial \tilde V}{\partial p}\right)_T$	[illegible]	$-\left(\frac{\partial \tilde V}{\partial T}\right)_p$
p	-1	~	$-\left(\frac{\partial \tilde V}{\partial T}\right)_p$	$-\tilde C_p + p\left(\frac{\partial \tilde V}{\partial T}\right)_p$	$-\frac{\tilde C_p}{T}$
$\tilde V$	$-\left(\frac{\partial \tilde V}{\partial p}\right)_T$	$\left(\frac{\partial \tilde V}{\partial T}\right)_p$	~	$-T\left(\frac{\partial \tilde V}{\partial T}\right)_p^2 - \tilde C_p\left(\frac{\partial \tilde V}{\partial p}\right)_T$	[illegible]
$\tilde U$	$T\left(\frac{\partial \tilde V}{\partial T}\right)_p + p\left(\frac{\partial \tilde V}{\partial p}\right)_T$	$\tilde C_p - p\left(\frac{\partial \tilde V}{\partial T}\right)_p$	[illegible]	~	$p\left(\frac{\partial \tilde V}{\partial T}\right)_p^2 + \frac{p\tilde C_p}{T}\left(\frac{\partial \tilde V}{\partial p}\right)_T$
$\tilde S$	$\left(\frac{\partial \tilde V}{\partial T}\right)_p$	$\frac{\tilde C_p}{T}$	$\left(\frac{\partial \tilde V}{\partial T}\right)_p^2 + \frac{\tilde C_p}{T}\left(\frac{\partial \tilde V}{\partial p}\right)_T$	$-p\left(\frac{\partial \tilde V}{\partial T}\right)_p^2 - \frac{p\tilde C_p}{T}\left(\frac{\partial \tilde V}{\partial p}\right)_T$	~

by the value of the Jacobian in Table 1-1 in which the first letter of the first line is the quantity with respect to which the differentiation is taking place and in which the second letter in the first line is the quantity held constant.

To obtain the relation among any four derivatives, having expressed them in terms of the same three derivatives, $\left(\frac{\partial V}{\partial T}\right)_p$, $\left(\frac{\partial V}{\partial p}\right)_T$, and c_p, one has only to eliminate the three derivatives from the four equations, leaving a single equation connecting the four derivatives.

Three functions used in thermodynamics to facilitate the solution of many problems are the following: the enthalpy H, defined by the equation $H \equiv U + pV$, the Helmholtz function A, defined by the equation $A \equiv U - TS$, and the Gibbs function G, defined by the equation $G \equiv U + pV - TS$. The corresponding specific functions are H, A, and G. Partial derivatives involving one or more of the functions H, A, and G, can also be calculated as the quotients of two Jacobians, which can themselves be calculated by the same method used to calculate the Jacobians in Table 1-1.

Appendix A to Part I

Transformation of the work and heat line integrals from one coordinate plane to other coordinate planes in the case of a one-component system of one phase and of unit mass

The derivatives of the work done and the heat received by a one-component system of one phase and of unit mass are total derivatives[1] with respect to the variables chosen as the parameters defining the paths of the integrals. In order to obtain the total derivative of the work done along a straight line parallel to one of the coordinate axes in any plane, one obtains from Table 1-1 the partial derivative of the volume with respect to the quantity plotted along that axis when the quantity plotted along the other axis is held constant and one multiplies the partial derivative of the volume by the pressure. Similarly to obtain the total derivative of the heat received along a straight line parallel to one of the coordinate axes in any plane, one obtains from the table the partial derivative of the entropy with respect to the quantity plotted along that axis when the quantity plotted along the other axis is held constant and one multiplies the partial derivative of the entropy by the temperature. For example, the derivatives of the work done and heat received along a straight line parallel to the K-axis in the (7\ **7)-plane** are

$$(\S)_T - P \qquad (I\text{-}A\text{-}D$$

[1] **Tunell,** G., Jour. Chenu Physics, 9, 191-192, 1941,

and

$1= KDJ* (II- (I-A-2)

The total derivatives of the 'heat received along lines parallel to the coordinate axes in any desired plane can also be derived in terms of the total derivatives of the heat received along lines parallel to the coordinate axes in the *(T$* p)-plane by transformation of the heat line integral as explained in the second half of Appendix B to Part I. Following is an example of such a transformation. In the case of a one-component system of one phase and of unit mass the heat line integral extended along a path in the (7\ $\breve{F}$)-plane is

$$Q = \int_{T_0, \breve{V}_0}^{T, \breve{V}} \left\{ \left(\frac{dQ}{dT}\right)_{\breve{V}} dT + \left(\frac{dQ}{d\breve{V}}\right)_T d\breve{V} \right\}$$

$$= \int_{T_0, \breve{V}_0}^{T, \breve{V}} \left\{ \qquad + l_v d\breve{V} \right\}, \qquad \text{(I-A-3)}$$

where $\breve{c}_v$ denotes the heat capacity at constant volume per unit of mass and l_v denotes the latent heat of change of volume at constant temperature, and where $\breve{c}_v$ and l_v are functions of T and 7. This integral depends upon the path in the (T, V)-plane determined by an equation between T and $\breve{V}$, $T = f(\breve{V})$.

In this case 1-^H$_w$ / ("57r) • ^^{n} order to transform the /dl_v\ /3$\breve{c}_v$\

integral for Q from the $(T, \breve{V})$-plane to the (T, p)-plane, p denoting the pressure, we make use of the fact that $\breve{V}$ is a function of T and p,

$$\breve{V} = F(T, p). \qquad \text{(I-A-4)}$$

Thus we write for the integral transposed to the (T, p)-plane

$$Q = \int_{T_0,\,p_0}^{T,\,p} \left\{ \breve{c}_V dT + l_V \left(\left(\frac{\partial \breve{V}}{\partial T}\right)_p dT + \left(\frac{\partial \breve{V}}{\partial p}\right)_T dp \right) \right\}$$

$$= \int_{T_0,\,p_0}^{T,\,p} \left\{ \left(\breve{c}_V + l_V \left(\frac{\partial \breve{V}}{\partial T}\right)_p \right) dT + l_V \left(\frac{\partial \breve{V}}{\partial p}\right)_T dp \right\} . \qquad \text{(I-A-5)}$$

By definition the coefficients of dT and dp in this integral are $\breve{c}_p$ and $\breve{l}_p$. Thus we obtain the equations

$$\breve{c}_p = \breve{c}_V + l_V \left(\frac{\partial \breve{V}}{\partial T}\right)_p \qquad \text{(I-A-6)}$$

and

$$\breve{l}_p = l_V \left(\frac{\partial \breve{V}}{\partial p}\right)_T . \qquad \text{(I-A-7)}$$

From equations (I-A-6) and (I-A-7) we obtain $\breve{c}_V$ and l_V as functions of T and p:

$$\breve{c}_V = \breve{c}_p - \breve{l}_p \left(\frac{\partial \breve{V}}{\partial T}\right)_p \Big/ \left(\frac{\partial \breve{V}}{\partial p}\right)_T \qquad \text{(I-A-8)}$$

and

$$l_V = \breve{l}_p \Big/ \left(\frac{\partial \breve{V}}{\partial p}\right)_T . \qquad \text{(I-A-9)}$$

The same result can be obtained by substitution of values in equations (I-B-35) and (I-B-36) in Appendix B to Part I. The equivalence of symbols for the purpose of this substitution is given in the following Table.

Table I-A-l
Equivalence of symbols

r	o
x	T
y	$\breve{V}$
$P(x, y)$	$\left(\frac{dQ}{dT}\right)_{\breve{V}}$
$Q(x, y)$	$\left(\frac{dQ}{d\breve{V}}\right)_T$
u	T
v	p
θ(u, v)	$\breve{c}_p$
tt(u,v)	L_p

Substituting the values from the right hand column for the values in the left hand column in equations (I-B-35) and

(I-B-36) we have

$$\left(\frac{dQ}{dT}\right)_{\breve V} = \breve c_V = \frac{\breve c_p\left(\frac{\partial \breve V}{\partial p}\right)_T - \breve l_p\left(\frac{\partial \breve V}{\partial T}\right)_p}{1\cdot\left(\frac{\partial \breve V}{\partial p}\right)_T - 0\cdot\left(\frac{\partial \breve V}{\partial T}\right)_p}$$

$$= \left[\breve c_p\left(\frac{\partial \breve V}{\partial p}\right)_T + T\left(\frac{\partial \breve V}{\partial T}\right)_p^2\right] \div \left(\frac{\partial \breve V}{\partial p}\right)_T , \qquad \text{(I-A-10)}$$

and

$$\left(\frac{dQ}{d\breve V}\right)_T = \breve l_V = \frac{\breve c_p\cdot 0 - \breve l_p\cdot 1}{\left(\frac{\partial \breve V}{\partial T}\right)_p\cdot 0 - \left(\frac{\partial \breve V}{\partial p}\right)_T\cdot 1}$$

$$= \left[-T\left(\frac{\partial \breve V}{\partial T}\right)_p\right] \div \left(\frac{\partial \breve V}{\partial p}\right)_T . \qquad \text{(I-A-11)}$$

Finally, equations (I-A-8) and (I-A-10) are equivalent because

$$\breve l_p = -T\left(\frac{\partial \breve V}{\partial T}\right)_p .$$

Appendix B to Part I

Proofs of the relations:

$$\left(\frac{\partial x'}{\partial x}\right)_y = \frac{\dfrac{\partial(x', y)}{\partial(u, v)}}{\dfrac{\partial(x, y)}{\partial(u, v)}}$$

and

$$\left(\frac{\partial T}{\partial x}\right)_y = \frac{\begin{vmatrix} \dfrac{\partial T}{\partial u} & \dfrac{\partial T}{\partial v} \\ \dfrac{\partial y}{\partial u} & \dfrac{\partial y}{\partial v} \end{vmatrix}}{\begin{vmatrix} \dfrac{\partial x}{\partial u} & \dfrac{\partial x}{\partial v} \\ \dfrac{\partial y}{\partial u} & \dfrac{\partial y}{\partial v} \end{vmatrix}}$$

It is assumed that x' is a function of x and y,

$$x' = \psi(x, y) \qquad \text{(I-B-1)}$$

and that x and y are functions of u and v,

$$x = f(u, v), \qquad \text{(I-B-2)}$$

and

$$y = \phi(u, v). \qquad \text{(I-B-3)}$$

It is assumed further that these functions are continuous together with their first partial derivatives. By application of the theorem for change of variables in partial differentiation[1] one then obtains

$$\frac{\partial x'}{\partial u} = \frac{\partial x'}{\partial x}\frac{\partial x}{\partial u} + \frac{\partial x'}{\partial y}\frac{\partial y}{\partial u} \qquad \text{(I-B-4)}$$

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[1] Osgood, W.F., *Advanced Calculus,* The MacMillan Co., New York, 1925, pp. 112-115; Taylor, Angus, *Advanced Calculus,* Ginn and Co., Boston, New York, Chicago, Atlanta, Dallas, Palo Alto, Toronto, London, 1955, pp. 167-172.

and

$$\frac{\partial x'}{\partial v} = \frac{\partial x'}{\partial x}\frac{\partial x}{\partial v} + \frac{\partial x'}{\partial y}\frac{\partial y}{\partial v} \quad . \qquad \text{(I-B-5)}$$

From equations (I-B-4) and (I-B-5) it follows that

$$\frac{\partial x'}{\partial y}\frac{\partial y}{\partial u} = \frac{\partial x'}{\partial u} - \frac{\partial x'}{\partial x}\frac{\partial x}{\partial u} \qquad \text{(I-B-6)}$$

and

$$\frac{\partial x'}{\partial y}\frac{\partial y}{\partial v} = \frac{\partial x'}{\partial v} - \frac{\partial x'}{\partial x}\frac{\partial x}{\partial v} \quad . \qquad \text{(I-B-7)}$$

Dividing both sides of equation (I-B-6) by $\frac{\partial y}{\partial u}$ and both sides of equation (I-B-7) by $\frac{\partial y}{\partial v}$ we have

$$\frac{\partial x'}{\partial y} = \frac{\frac{\partial x'}{\partial u} - \frac{\partial x'}{\partial x}\frac{\partial x}{\partial u}}{\frac{\partial y}{\partial u}} \qquad \text{(I-B-8)}$$

and

$$\frac{\partial x'}{\partial y} = \frac{\frac{\partial x'}{\partial v} - \frac{\partial x'}{\partial x}\frac{\partial x}{\partial v}}{\frac{\partial y}{\partial v}} \quad . \qquad \text{(I-B-9)}$$

It follows that the right side of equation (I-B-8) is equal to the right side of equation (I-B-9)

$$\frac{\frac{\partial x'}{\partial u} - \frac{\partial x'}{\partial x}\frac{\partial x}{\partial u}}{\frac{\partial y}{\partial u}} = \frac{\frac{\partial x'}{\partial v} - \frac{\partial x'}{\partial x}\frac{\partial x}{\partial v}}{\frac{\partial y}{\partial v}} \quad . \qquad \text{(I-B-10)}$$

Multiplying both sides of equation (I-B-10) by $\left(\frac{\partial y}{\partial u}\frac{\partial y}{\partial v}\right)$ we have

$$\frac{\partial y}{\partial v}\left(\frac{\partial x'}{\partial u} - \frac{\partial x'}{\partial x}\frac{\partial x}{\partial u}\right) = \frac{\partial y}{\partial u}\left(\frac{\partial x'}{\partial v} - \frac{\partial x'}{\partial x}\frac{\partial x}{\partial v}\right) \qquad \text{(I-B-11)}$$

and consequently

$$\frac{\partial y}{\partial v}\frac{\partial x'}{\partial u} - \frac{\partial y}{\partial v}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial u} = \frac{\partial y}{\partial u}\frac{\partial x'}{\partial v} - \frac{\partial y}{\partial u}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial v} . \qquad \text{(I-B-12)}$$

From equation (I-B-12) it follows that

$$\frac{\partial x'}{\partial x}\frac{\partial y}{\partial u}\frac{\partial x}{\partial v} - \frac{\partial x'}{\partial x}\frac{\partial y}{\partial v}\frac{\partial x}{\partial u} = \frac{\partial y}{\partial u}\frac{\partial x'}{\partial v} - \frac{\partial y}{\partial v}\frac{\partial x'}{\partial u} \qquad \text{(I-B-13)}$$

and

$$\frac{\partial x'}{\partial x}\left(\frac{\partial y}{\partial u}\frac{\partial x}{\partial v} - \frac{\partial y}{\partial v}\frac{\partial x}{\partial u}\right) = \frac{\partial y}{\partial u}\frac{\partial x'}{\partial v} - \frac{\partial y}{\partial v}\frac{\partial x'}{\partial u} . \qquad \text{(I-B-14)}$$

Dividing both sides of equation (I-B-14) by $\left(\frac{\partial y}{\partial u}\frac{\partial x}{\partial v} - \frac{\partial y}{\partial v}\frac{\partial x}{\partial u}\right)$ we have

$$\left(\frac{\partial x'}{\partial x}\right)_y = \frac{\frac{\partial y}{\partial u}\frac{\partial x'}{\partial v} - \frac{\partial y}{\partial v}\frac{\partial x'}{\partial u}}{\frac{\partial y}{\partial u}\frac{\partial x}{\partial v} - \frac{\partial y}{\partial v}\frac{\partial x}{\partial u}} . \qquad \text{(I-B-15)}$$

The partial derivative $\left(\frac{\partial x'}{\partial x}\right)_y$ is thus equal to the quotient of two Jacobian determinants

$$\left(\frac{\partial x'}{\partial x}\right)_y = \frac{\begin{vmatrix} \frac{\partial x'}{\partial u} & \frac{\partial x'}{\partial v} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} \end{vmatrix}}{\begin{vmatrix} \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} \end{vmatrix}} , \qquad \text{(I-B-16)}$$

provided the Jacobian determinant in the denominator is not equal to zero. Thus we obtain the result

$$\left(\frac{\partial x'}{\partial x}\right)_y = \frac{\dfrac{\partial(x', y)}{\partial(u, v)}}{\dfrac{\partial(x, y)}{\partial(u, v)}} \qquad \text{(I-B-17)}$$

and similarly we have

$$\left(\frac{\partial x'}{\partial y}\right)_x = \frac{\dfrac{\partial(x', x)}{\partial(u, v)}}{\dfrac{\partial(y, x)}{\partial(u, v)}} . \qquad \text{(I-B-18)}$$

This case corresponds to the case of a one-component system of one phase and of unit mass in which it is desired to transform a function of the coordinates, such as the volume, the energy, or the entropy, from one coordinate plane, such as the entropy-volume plane to another coordinate plane, such as the temperature-pressure plane.

Equations (I-B-17) and (I-B-18) are not applicable, however, in the case of a one-component system of one phase and of unit mass when it is desired to transform the work line integral or the heat line integral from one coordinate plane, such as the entropy-volume plane, to another coordinate plane, such as the temperature-pressure plane, because the work line integral and the heat line integral depend upon the path and are not functions of the coordinates. In this case, to which the second equation of the heading of this Appendix applies, the transformation can be accomplished in the following way. Let us suppose that a line integral Γ

$$\Gamma = \int_{x_0, y_0}^{x, y} \{P(x, y)dx + Q(x, y)dy\} \qquad \text{(I-B-19)}$$

depends upon the path in which case $\frac{\partial P}{\partial y} \neq \frac{\partial Q}{\partial x}$. This integral has no meaning unless a further relation is given between x and y, $y = f(x)$, defining a particular path in the (x, y)-plane.[2] We are next given that x and y are functions of u and v,

$$x = \phi(u, v), \qquad \text{(I-B-20)}$$

and

$$y = \psi(u, v). \qquad \text{(I-B-21)}$$

It is then desired to transform the integral Γ from the

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[2] In general this curve can be represented in parametric form, $x = X(\sigma)$, $y = Y(\sigma)$, but in simple cases the curve can be expressed by the equation $y = f(x)$, or at least in segments by the equations $y' = f(x)$, $y'' = F(x)$.

(x, y)-plane to the (u, v)-plane.[3] In this case if equations (I-B-20) and (I-B-21) can be solved so that we have

$$u = \Phi(x, y), \tag{I-B-22}$$

and

$$v = \Psi(x, y), \tag{I-B-23}$$

then the curve in the (x, y)-plane can be transformed into the curve in the (u, v)-plane defined by the equation $u = F(v)$.

We next replace dx in the integral T by $\frac{\partial x}{\partial u} du + \frac{\partial x}{\partial v} dv$ and dy by $\frac{\partial y}{\partial u} du + \frac{\partial y}{\partial v} dv$. We then have

$$T = \int_{u_0, v_0}^{u, v} \left\{ P \left[\frac{\partial x}{\partial u} du + \frac{\partial x}{\partial v} dv \right] + Q \left[\frac{\partial y}{\partial u} du + \frac{\partial y}{\partial v} dv \right] \right\}, \tag{I-B-24}$$

the curve in the (u, v)-plane now being determined by the

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[3] Cf. R. Courant, *Differential and Integral Calculus,* Translated by J.E. McShane, Blackie & Son Ltd., London and Glasgow, 1944, Vol. 2, p. 373. The procedure for transforming a line integral that depends upon the path from the (x, y)-plane to the (u, v)-plane used by Courant is the same as the procedure explained here and in Appendix C to Part II of this text.

equation $u = F(v)$. Consequently we thus obtain

$$\Gamma = \int_{u_0,\, v_0}^{u,\, v} \left\{ P(\phi(u, v), \psi(u, v)) \left[\frac{\partial x}{\partial u} du + \frac{\partial x}{\partial v} dv \right] \right.$$

$$\left. + \; Q(\phi(u, v), \psi(u, v)) \left[\frac{\partial y}{\partial u} du + \frac{\partial y}{\partial v} dv \right] \right\}$$

$$= \int_{u_0,\, v_0}^{u,\, v} \left\{ \left[P(\phi(u, v), \psi(u, v)) \frac{\partial x}{\partial u} + Q(\phi(u, v), \psi(u, v)) \frac{\partial y}{\partial u} \right] du \right.$$

$$\left. + \; \left[P(\phi(u, v), \psi(u, v)) \frac{\partial x}{\partial v} + Q(\phi(u, v), \psi(u, v)) \frac{\partial y}{\partial v} \right] dv \right\}$$

$$= \int_{u_0,\, v_0}^{u,\, v} \{ \Phi(u, v)\, du + Q(u, v)\, dv \} \quad , \qquad \text{(I-B-25)}$$

where Φ is set equal to

$$\left[P(\phi(u, v), \psi(u, v)) \frac{\partial x}{\partial u} + Q(\phi(u, v), \psi(u, v)) \frac{\partial y}{\partial u} \right]$$

and Q is set equal to

$$\left[P(\phi(u,v),\psi(u,v))\frac{\partial x}{\partial v}+Q(\phi(u,v),\psi(u,v))\frac{\partial y}{\partial v}\right] .$$

In order to evaluate P and Q as functions of u and v we next solve the equations

$$\Theta = P\frac{\partial x}{\partial u} + Q\frac{\partial y}{\partial u} \qquad \text{(I-B-26)}$$

and

$$\Omega = P\frac{\partial x}{\partial v} + Q\frac{\partial y}{\partial v} \qquad \text{(I-B-27)}$$

for P and Q. Thus we have

$$Q\frac{\partial y}{\partial u} = \Theta - P\frac{\partial x}{\partial u} \qquad \text{(I-B-28)}$$

and

$$Q\frac{\partial y}{\partial v} = \Omega - P\frac{\partial x}{\partial v} . \qquad \text{(I-B-29)}$$

Dividing both sides of equation (I-B-28) by $\frac{\partial y}{\partial u}$ and both sides of equation (I-B-29) by $\frac{\partial y}{\partial v}$ we obtain

$$Q = \Theta\Big/\frac{\partial y}{\partial u} - P\frac{\partial x}{\partial u}\Big/\frac{\partial y}{\partial u} \qquad \text{(I-B-30)}$$

and

$$Q = \Omega\Big/\frac{\partial y}{\partial v} - P\frac{\partial x}{\partial v}\Big/\frac{\partial y}{\partial v} \qquad \text{(I-B-31)}$$

and consequently

$$\Theta\Big/\frac{\partial y}{\partial u} - P\frac{\partial x}{\partial u}\Big/\frac{\partial y}{\partial u} = \Omega\Big/\frac{\partial y}{\partial v} - P\frac{\partial x}{\partial v}\Big/\frac{\partial y}{\partial v} . \qquad \text{(I-B-32)}$$

From equation (I-B-32) it follows that

$$P\frac{\partial x}{\partial u}\Big/\frac{\partial y}{\partial u} - P\frac{\partial x}{\partial v}\Big/\frac{\partial y}{\partial v} = \Theta\Big/\frac{\partial y}{\partial u} - \Omega\Big/\frac{\partial y}{\partial v} . \qquad \text{(I-B-33)}$$

Thus from equation (I-B-33) we obtain the value of P as a function of u and v:

$$P = \frac{\Theta\Big/\frac{\partial y}{\partial u} - \Omega\Big/\frac{\partial y}{\partial v}}{\frac{\partial x}{\partial u}\Big/\frac{\partial y}{\partial u} - \frac{\partial x}{\partial v}\Big/\frac{\partial y}{\partial v}} \qquad \text{(I-B-34)}$$

and multiplying both numerator and denominator of the right side of equation (I-B-34) by $\left(\frac{\partial y}{\partial u}\frac{\partial y}{\partial v}\right)$ we have

$$P = \frac{\Theta\frac{\partial y}{\partial v} - \Omega\frac{\partial y}{\partial u}}{\frac{\partial x}{\partial u}\frac{\partial y}{\partial v} - \frac{\partial x}{\partial v}\frac{\partial y}{\partial u}} . \qquad \text{(I-B-35)}$$

Now $P(x, y)$ is the total derivative of T along a line parallel to the x-axis in the (x, y)-plane.[4] Also $\Theta(u, v)$ is the total

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[4] Cf. G. Tunell, Jour. Chem. Physics, 9, 191-192, 1941.

derivative of T along a line parallel to the u-axis in the (u, v)-plane and $Q(u, v)$ is the total derivative of T along a line parallel to the v-axis in the (u, v)-plane. Thus from equation (I-B-35) we have

$$P(x, y) = \left(\frac{dT}{dx}\right)_y = \frac{\begin{vmatrix} \frac{dT}{du} & \frac{dT}{dv} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} \end{vmatrix}}{\begin{vmatrix} \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} \end{vmatrix}} . \qquad \text{(I-B-36)}$$

Likewise $Q(x, y)$ is the total derivative of T along a line parallel to the y-axis in the (x, y)-plane. Thus in a similar way we have

$$Q(x, y) = \left(\frac{dT}{dy}\right)_x = \frac{\begin{vmatrix} \frac{dT}{du} & \frac{dT}{dv} \\ \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} \end{vmatrix}}{\begin{vmatrix} \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} \\ \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} \end{vmatrix}} . \qquad \text{(I-B-37)}$$

The determinants forming the numerators of the fractions constituting the right sides of equations (I-B-36) and (I-B-37) are similar in form to the Jacobian determinants used in the transformation of functions of two or more variables, but F is not a function of x and y or of u and v and the derivatives in the top lines of the determinants constituting the numerators of the fractions that form the right sides of equations (I-B-36) and (I-B-37) are total derivatives, not partial derivatives.

Appendix C to Part I

Discussion of P.W. Bridgman's explanation of the derivation of the functions tabulated in his book entitled *A Condensed Collection of Thermodynamic Formulas*[1]

Bridgman explained the derivation of the functions tabulated in his book entitled *A Condensed Collection of Thermodynamic Formulas* in the following way.

> All the first derivatives are of the type $\left(\frac{\partial x_1}{\partial x_2}\right)_{x_3}$ where x_x, x_2, and X3 are any three *different* variables selected from the fundamental set (for example, p, T, *v)*. The meaning of the notation is the conventional one in thermodynamics, the subscript X3 denoting that the variable x_3 is maintained constant, and the ratio of the change of *x* to the change of *X2* calculated under these conditions. The restrictions imposed by the physical nature of the system are such that derivatives of this type have a unique meaning. The number of such first derivatives evidently depends on the number of quantities selected as fundamental. For nearly all applications 10 such variables are sufficient, and this is the number taken for these tables. ...[2]
>
> Given now 10 fundamental quantities, there are 10x9x8 = 720 first derivatives. A complete collection of thermodynamic formulas for first derivatives includes all possible relations between these 720

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[1] Harvard University Press, Cambridge, 1925.

[2] The variables selected as fundamental by Bridgman are the following: the pressure p, the temperature T, the volume v, the entropy s, the heat Q, the work *w,* the energy £, the enthalpy #, the Gibbs function *z* , and the Helmholtz function ¥.

derivatives. In general, the relations involve any four of the derivatives, for any three of the derivatives are independent of each other. (There are, of course, a large number of degenerate cases in which there are relations between fewer than four derivatives.) Now, except for the degenerate cases, the number of relations between first derivatives is the number of ways in which 4 articles can be selected from 720, or

$$\frac{720 \times 719 \times 718 \times 717}{1 \times 2 \times 3 \times 4} = \text{approx. } 11 \times 10^9 .$$

This is the number of thermodynamic relations which should be tabulated in a complete set of formulas, but such a programme is absolutely out of the question. We can, however, make it possible to obtain at once any one of the 11×10^9 relations if we merely tabulate every one of the 720 derivatives in terms of the same set of three. For to obtain the relation between any four derivatives, having expressed them in terms of the same fundamental three, we have only to eliminate the fundamental three between the four equations, leaving a single equation connecting the desired four derivatives.

This programme involves the tabulating of 720 derivatives, and is not of impossible proportions. But this number may be much further reduced by mathematical artifice. The 720 derivatives fall into 10 groups, all the derivatives of a group having the same variable held constant during the differentiation. Now each of the 72 derivatives in a group may be completely expressed in terms of only 9 quantities. Consider for example the first group, in which x_1 is the variable kept constant. Then any derivative of this group $\left(\frac{\partial x_j}{\partial x_k}\right)_{x_1}$ may be written in the form $\left(\frac{\partial x_j}{\partial x_k}\right)_{x_1} = \left(\frac{\partial x_j}{\partial \alpha}\right)_{x_1} \Big/ \left(\frac{\partial x_k}{\partial \alpha}\right)_{x_1}$, where α is any new variable, not necessarily one of the 10. Let us make this transformation for all the derivatives of the group, keeping the same α in all the transformations. Then it is evident that all derivatives of the group may be expressed in terms of the nine derivatives $\left(\frac{\partial x_2}{\partial \alpha}\right)_{x_1}$ $\cdots$ $\left(\frac{\partial x_{10}}{\partial \alpha}\right)_{x_1}$. By taking the ratio of the appropriate pair. That is, for the purpose of calculating the derivatives we may replace the derivative $\left(\frac{\partial x_j}{\partial x_k}\right)_{x_1}$ by the ratio of numerator to denominator, writing

$$\left(\frac{\partial x_j}{\partial x_k}\right)_{x_1} \equiv \frac{(\partial x_j)_{x_1}}{(\partial x_k)_{x_1}}$$

and then substitute for $(\partial x_j)_{x_1}$ the finite derivative $\left(\frac{\partial x_j}{\partial \alpha}\right)_{x_1}$ and for $(\partial x_k)_{x_1}$, $\left(\frac{\partial x_k}{\partial \alpha}\right)_{x_1}$.

We may now, as a short-hand method of expression, write the equations

$$(\partial x_j)_{x_1} = \left(\frac{\partial x_j}{\partial \alpha}\right)_{x_1}, \text{ etc.,}$$

remembering, however, that this is not strictly an equation at all (the dimensions of the two sides of the "equation" are not the same), but that the form of expression is useful because the correct result is always obtained when the ratio of two such differentials is taken.

We may proceed in this way systematically through the remaining 9 groups of 72 derivatives, choosing a new and arbitrary α for each group. We will thus have in all 90 different expressions to tabulate. This number may now be further reduced to 45 by so choosing the α's in the successive groups that the condition $(\partial x_i)_{x_j} = -(\partial x_j)_{x_i}$ is satisfied. That such a choice is possible requires proof, for having once chosen α_1, the choice of α_2 is fixed by the requirement that $(\partial x_1)_{x_2} = -(\partial x_2)_{x_1}$, and α_3 is fixed by the requirement that $(\partial x_1)_{x_3} = -(\partial x_3)_{x_1}$, so that it is now a question whether these values of α_2 and α_3 are such that $(\partial x_2)_{x_3} = -(\partial x_3)_{x_2}$. That these conditions are compatible is an immediate consequence of the mathematical identity

$$\left(\frac{\partial x_1}{\partial x_2}\right)_{x_3} \cdot \left(\frac{\partial x_2}{\partial x_3}\right)_{x_1} \cdot \left(\frac{\partial x_3}{\partial x_1}\right)_{x_2} = -1.$$

The only degree of arbitrariness left is now in α_1, which may be chosen to make the expressions as simple as possible.

In the actual construction of the tables the a's play no part, and in fact none of them need be determined; their use has been merely to show the possibility of writing a derivative as the quotient of two finite functions, one replacing the differential numerator, and the other the differential denominator. The tables were actually deduced by writing down a sufficient number of derivatives obtained by well-known thermodynamic methods, and then splitting these derivatives by inspection into the quotient of numerator and denominator. Having once fixed the value of a single one of the differentials arbitrarily, all the others are thereby fixed* For simplicity it was decided to put $(\partial x)_p = 1$.

The choice of the fundamental three derivatives leaves much latitude. It seemed best to take three which are given directly by ordinary experiment; the three chosen are

$$\left(\frac{\partial v}{\partial T}\right)_p, \left(\frac{\partial v}{\partial p}\right)_T, \text{ and } c_p \left[= \left(\frac{\partial Q}{\partial T}\right)_p\right].$$

The problem addressed by Bridgman is that of obtaining a derivative of any one variable of the 10 variables with respect to any second variable of the 10 when any third variable of the 10 is held constant in terms of the three derivatives $\left(\frac{\partial v}{\partial T}\right)_p$, $\left(\frac{\partial v}{\partial p}\right)_T$, and c_p, and certain of the thermodynamic quantities. This is a problem of obtaining derivatives with respect to a new set of independent variables in terms of derivatives with respect to an original set of independent variables. The solution of this problem by means of Jacobians was given by Bryan[3] in his article in the *Encyclopädie der matematischen Wissenschaften* in 1903 and is well established. The functions listed by Bridgman in his table as $(\partial p)_v$, $(\partial T)_v$, $(\partial S)_v$, $(\partial E)_v$, $(\partial p)_s$, $(\partial T)_s$, $(\partial V)_s$, $(\partial E)_s$, etc., are really Jacobians, not partial derivatives with respect to hypothetical auxiliary variables α_3, α_4. In the derivation by means of Jacobians explained in the preceding pages no hypothetical auxiliary variables were involved and likewise no hypothetical unknown functions of α_1 and p, or of α_2 and T, or of α_3 and *v*, etc., were involved. Furthermore it is really not a matter of hypothesis that $(\partial x_1)_{x_2} = -(\partial x_2)_{x_1}$. The quantity $(\partial x_1)_{x_2}$ is really the Jacobian $\frac{\partial(x_1, x_2)}{\partial(T, p)}$ and the quantity $(\partial x_2)_{x_1}$ is really the Jacobian $\frac{\partial(x_2, x_1)}{\partial(T, p)}$. The Jacobian $\frac{\partial(x_1, x_2)}{\partial(T, p)}$ is equal to the negative of the Jacobian $\frac{\partial(x_2, x_1)}{\partial(T, p)}$ because interchanging two rows of a determinant changes the sign of the determinant. Finally it is not an arbitrarily adopted convention that $(\partial T)_p = 1$. The quantity $(\partial T)_p$ is equal to the Jacobian $\frac{\partial(T, p)}{\partial(T, p)}$ which is automatically equal to 1.

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[3] Bryan, G.H., in *Encyclopädie der matematischen Wissenschaften*, B.G. Teubner, Leipzig, Bd. V, Teil 1, S. 113, 1903.

Part II

Relations between thermodynamic quantities and their first derivatives in a one-component system of one phase and of variable mass

Introduction

Thermodynamic relations in open systems of one component and of one phase and other open systems have been analyzed by Gillespie and Coe,[1] Van Wylen,[2] Hall and Ibele,[3] and Beattie and Oppenheim,[4] also in part incorrectly by Larmor,[5] Morey,[6] Goranson,[7] Sage,[8] Moelwyn-Hughes,[9] Callen,[10] and Wheeler.[11]

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[1] Gillespie, L.J., and J.R. Coe, Jr., Jour. Chem. Phys., 1, 103-113, 1933.

[2] Van Wylen, G.J., *Thermodynamics,* John Wiley and Sons, Inc., New York, Chapman and Hall, London, 1959.

[3] Hall, N.A., and W.E. Ibele, *Engineering Thermodynamics,* Prentice-Hall, Inc., Englewood-Cliffs, N.J., 1960.

** Beattie, J.A., and Irwin Oppenheim, *Principles of Thermodynamics,* Elsevier Scientific Publishing Co., Amsterdam, Oxford, New York, 1979, pp. 296-320.

[5] Larmor, Sir Joseph, Proc. Roy. Soc. London, 75, 280-296, 1905.

[5] Morey, G.W., Jour. Franklin Inst., 194, 425-484, 1922.

[7] Goranson, R.W., *Thermodynamic Relations in Multi-Component Systems,* Carnegie Institution of Washington Publication No. 408, 1930.

[8] Sage, B.H., *Thermodynamics of Multicomponent Systems,* Reinhold Publishing Corp., New York, 1965.

[9] Moelwyn-Hughes, E.A., *Physical Chemistry,* Pergamon Press, London, New York, Paris, 1957.

[10] Callen, H.E., *Thermodynamics,* John Wiley and Sons, Inc., New York and London, 1960.

[11] Wheeler, L.P., *Josiah Willard Gibbs - The History of a Great Mind,* Rev. Ed., Yale University Press, Mew Haven, 1952,

In the following text the relations for the energy and the entropy of a one-component system of one phase and of variable mass are derived and a table of Jacobians is presented by means of which any first partial derivative of any one of the quantities, the absolute thermodynamic temperature *T,* the pressure p, the total mass M_f the total volume *V ,* the total energy *U,* and the total entropy 5, with respect to any other of these quantities can be obtained in terms of the partial derivative of the specific volume with respect to the temperature, the partial derivative of the specific volume with respect to the pressure, the heat capacity at constant pressure per unit of mass, and certain of the quantities 7\ p, Aft *V, U, S.*

In the case of a one-component system of one phase and of variable mass it is not necessary to make use of a definition of heat or a definition of work in the case of an open system when mass is being transferred to or from the system in order to derive the relations for the total energy and the total entropy. For some purposes, however, it has been found useful to have definitions of heat and work in the case of open systems when mass is being transferred to or from the system. The definitions of heat and work in the case of open systems used by various authors are discussed in Appendix A to Part II.

Calculation of the total volume, the total energy, and the total entropy of a one-component system of one phase and of variable mass as functions of the absolute thermodynamic temperature, the pressure, and the total mass

Thermodynamic formulas can be developed in the case of a one-component system of one phase and of variable mass on the basis of the following set of variable quantities: the absolute thermodynamic temperature T_t the pressure P, the

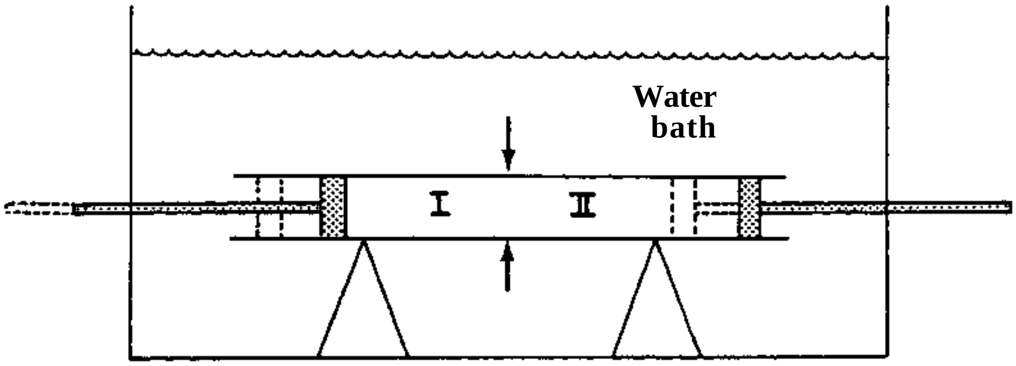

Figure II-1

total mass M, the total volume V, the total energy U, the total entropy S, the specific volume $\breve{V}$, the specific energy $\breve{U}$, the specific entropy $\breve{S}$, the heat capacity at constant pressure per unit of mass $\breve{C}_p$, and the latent heat of change of pressure at constant temperature per unit of mass $\breve{l}_p$. Two one-component systems of one phase and of variable mass are illustrated in Figure II–1. The formulas developed in the following pages apply to either open system I or open system II in Figure II–1. Open systems I and II together constitute a closed system.

In the case of a one-component system of one phase and of variable mass the total volume V is a function of the absolute thermodynamic temperature T, the pressure p, and the total mass M

$$V = f(T, p, M) \ . \qquad \text{(II-1)}$$

The total volume is equal to the total mass times the specific volume

$$V = M\breve{V} \ , \qquad \text{(II-2)}$$

and the specific volume is a function of the absolute thermodynamic temperature and the pressure,

$$\breve{V} = \phi(T, p) \ . \qquad \text{(II-3)}$$

From equations (II-1), (II-2), and (II-3) it follows that

$$\left(\frac{\partial V}{\partial T}\right)_{p,M} = M\left(\frac{\partial \breve{V}}{\partial T}\right)_p \ . \qquad \text{(II-4)}$$

$$\left(\frac{\partial V}{\partial p}\right)_{T,\,M} = M\left(\frac{\partial \breve{V}}{\partial p}\right)_T \;, \tag{II-5}$$

and

$$\left(\frac{\partial V}{\partial M}\right)_{T,\,p} = \breve{V} \;. \tag{II-6}$$

The total energy is a function of the absolute thermodynamic temperature, the pressure, and the total mass

$$U = MT,\ p,\ M) \;. \qquad \text{(H-7)}$$

It is known that the total energy of a one-component system of one phase and of variable mass is proportional to the total mass at a given temperature and a given pressure because it requires *M* times as much heat received and *M* times as much work done to take *M* times as much substance from the standard state to the given state as to take unit mass of the substance from the standard state to the given state through the same set of intermediate states. Thus the total energy is equal to the total mass times the specific energy

$$U = M\breve{U} \;. \tag{II-8}$$

Furthermore it is known from the case of a one-component system of one phase and of unit mass discussed in part I that the specific energy is a function of the absolute thermodynamic temperature and the pressure

$$\breve{U} = 8(T,\ p) \;. \qquad \text{(H-9)}$$

Thus the relation of the total energy to the absolute thermodynamic temperature, the pressure, and the total mass is expressed by the equation

$$U(T, p, M) - U(T_0, p_0, M_0)$$

$$= \int_{T_0, p_0, M_0} \left\{ M\left[\breve{c}_p - p\frac{\partial \breve{V}}{\partial T}\right]dT + M\left[\breve{l}_p - p\frac{\partial \breve{V}}{\partial p}\right]dp + \breve{U}dM \right\}. \qquad \text{(II-10)}$$

From equations (II-7), (II-8), (II-9), and (11-10) it follows that

$$\left(\frac{\partial U}{\partial T}\right)_{p,M} = M\left[\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right], \qquad \text{(II-11)}$$

$$\left(\frac{\partial U}{\partial p}\right)_{T,M} = M\left[\breve{l}_p - p\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right], \qquad \text{(II-12)}$$

and

$$\left(\frac{\partial U}{\partial M}\right)_{T,p} = \breve{U}. \qquad \text{(II-13)}$$

The total entropy is a function of the absolute thermodynamic temperature, the pressure, and the total mass

$$S = S(T, p, M). \qquad \text{(II-14)}$$

It is known that the total entropy of a one-component system of one phase and of variable mass is proportional to the total mass at a given temperature and a given pressure because it requires M times as much heat received to take M times as much substance from the standard state to the given state as to take unit mass of the substance from the standard state to the given state reversibly through the same set of intermediate states. Thus the total entropy is equal to the total mass times the specific entropy

$$S = M\breve{S} \; . \tag{11-15}$$

Furthermore it is known from the case of a one-component system of one phase and of unit mass discussed in Part I that the specific entropy is a function of the absolute thermodynamic temperature and the pressure

$$S = oo(T, p) \; . \tag{11-16}$$

Thus the relation of the total entropy to the absolute thermodynamic temperature, the pressure, and the total mass is expressed by the equation

$$S(T, p, M) - S(T_0, p_0, M_0)$$

$$= \int_{T_0, p_0, M_0}^{T, p, M} \left\{ M \frac{\breve{c}_p}{T} dT + M \breve{f} dp + \breve{S} dM \right\} \; . \tag{11-17}$$

From equations (11-14), (11-15), (11-16), and (11-17) it

follows that

$$\left(\frac{\partial S}{\partial T}\right)_{p,\,M} = M\frac{\breve{c}_p}{T}, \tag{II-18}$$

$$\left(\frac{\partial S}{\partial p}\right)_{T,\,M} = M\frac{\breve{l}_p}{T}, \tag{II-19}$$

and

$$\left(\frac{\partial S}{\partial M}\right)_{T,\,p} = \breve{S}. \tag{II-20}$$

It is to be noted that the derivations of equations (11-10) and (11-17) do not depend on definitions of heat and work in the case of open systems.[12] In equation (11-10) the coefficient of dT is the partial derivative of the total energy with respect to temperature at constant pressure and constant mass, which is known from the case of a one-component one-phase closed system to be $M\left[\breve{c}_p - p\left(\frac{\partial \breve{v}}{\partial T}\right)_p\right]$. Likewise the coefficient of dp in equation (11-10) is the partial derivative of the total energy with respect to pressure at constant temperature and constant mass, which is known from the case of a one-component one-phase closed system to be $M\left[\breve{l}_p - p\left(\frac{\partial \breve{v}}{\partial p}\right)_T\right]$. The coefficient of dM in equation (11-10) is

[12] It is possible to define heat and work in the case of a one-component system of one phase and of variable mass and this has been found to have usefulness in some engineering problems. See Appendix A to Part II.

the partial derivative of the total energy with respect to mass, which is simply the specific energy, because the addition of mass is at constant temperature and constant pressure. Likewise in equation (11-17) the coefficient of dT is the partial derivative of the total entropy with respect to temperature at constant pressure and constant mass, which is known from the case of a one-component one-phase closed system to be $M\frac{c_p}{T}$. Also in equation (11-17) the coefficient of dp is the partial derivative of the total entropy with respect to pressure at constant temperature and constant mass, which is known from the case of a one-component one-phase closed system to be $M\frac{\breve{l}_p}{T}$. The coefficient of dM in equation (11-17) is the partial derivative of the total entropy with respect to mass, which is simply the specific entropy, because the addition of mass is at constant temperature and constant pressure.

Necessary and sufficient conditions for (11-10) to be true are

$$\left\{\frac{\partial\left[M\left(\breve{l}_p - p\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right)\right]}{\partial T}\right\}_{p,M} = \left\{\frac{\partial\left[M\left(\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right)\right]}{\partial p}\right\}_{T,M}, \quad \text{(II-21)}$$

$$\left(\frac{\partial U}{\partial T}\right)_{p,M} = \left\{\frac{[\text{illegible}]\Big)_p\Big]}{\partial M}\right\}. \quad \text{(n-22)}$$

and

$$\left(\frac{\partial U}{\partial p}\right)_{T, M} = \left\{\frac{\partial\left[M\left(\breve{l}_p - p\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right)\right]}{\partial M}\right\}_{T, p} . \tag{II-23}$$[13]

Similarly, necessary and sufficient conditions for (II-17) to be true are

$$\left(\frac{\partial\left(M\frac{\breve{l}_p}{T}\right)}{\partial T}\right)_{p, M} = \left(\frac{\partial\left(M\frac{\breve{c}_p}{T}\right)}{\partial p}\right)_{T, M} , \tag{II-24}$$

$$\left(\frac{\quad}{\partial T}\right)_{p, M} = \left(\frac{\partial\left(M\frac{\breve{c}_p}{T}\right)}{\partial M}\right)_{T, p} , \tag{II-25}$$

and

$$\left(\frac{\partial S}{\partial p}\right)_{T, M} = \left(\frac{\partial\left(M\frac{\breve{l}_p}{T}\right)}{\partial M}\right)_{T, p} . \tag{II-26}$$

Carrying out the indicated differentiations in (II-21) and

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[13] Osgood, W.F., *Advanced Calculus*, The Macoillan Co., New York, 1925, p. 232, and Osgood, W.F., *Lehrbuch der Funktionentheorie*, B.G. Teubner, Leipzig, 5te Aufl., 1928, Bd. L, S. 142-150.

(11-24) one obtains

$$M \frac{p}{\partial T} \quad .. \quad 9F \qquad M 3 \breve{c}_p \qquad 8 \breve{y} \qquad 3\breve{F} \qquad ,TT\ 97,$$

and

$$M \frac{1}{T} \frac{\partial \breve{l}_p}{\partial T} - M \frac{\breve{l}_p}{T^2} = M \frac{1}{T} \frac{\partial \breve{c}_p}{\partial p} \ . \qquad \text{(II-28)}$$

Combining (11-27) and (11-28) one has

$$h = -r|£ \ . \qquad \text{(ii-29)}$$

From (11-27) and (11-29) it also follows that

$$\wedge_{\partial p} = -r|S_{\partial 1} \quad * \qquad \text{(II-30)}$$

From (11-22), (11-23), (11-25), and (11-26) only the already known equations

$$\frac{d\breve{U}}{df} = \tilde{\circ P} - p \frac{\partial \breve{V}}{\partial T} \ , \qquad \text{(II-31)}$$

$$\partial \breve{U} \qquad \breve{j} \qquad \partial \breve{V} \qquad /TT\ on\backslash$$

$$|\breve{f} = \breve{\wedge} \; ' \qquad \text{(II-33)}$$

and

$$I = \frac{\breve{l}_p}{T} , \qquad \text{(II-34)}$$

are derived,

Thus in order to obtain complete thermodynamic information for a one-component system of one phase and of variable mass it is only necessary to determine experimentally the specific volume as a function of temperature and pressure and the heat capacity at constant pressure per unit of mass as a function of temperature at one pressure. This is the same conclusion as the one reached by Bridgman[14] in the case of a one-component system of one phase and of constant mass. No additional measurements are required to obtain complete thermodynamic information for a one-component system of one phase and of variable mass beyond those required to obtain complete thermodynamic information for a one-component system of one phase and of constant mass.

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[14] Bricigroan, P.M., Phys. Rev., (2), 3, 274, 1914.

Derivation of any desired relation between the thermodynamic quantities T, p, M, V, U, S and their first derivatives for a one-component system of one phase and of variable mass by the use of functional determinants (Jacobians)

Equations (II-1), (II-10) and (II-17) can, in general, be solved for any three of the quantities, T, p, M, V, U, S, as functions of the remaining three. The first partial derivative of any one of the quantities, T, p, M, V, U, S with respect to any second quantity when any third and fourth quantities are held constant can be obtained in terms of the three first derivatives, $\left(\frac{\partial V}{\partial T}\right)_{p,M}$, $\left(\frac{\partial V}{\partial p}\right)_{T,M}$ and C_p, and certain of the quantities, T, p, M, V, U, S by application of the theorem[15] stating that, if $x' = \phi(x, y, z)$, $x = f(u, v, w)$, $y = \varphi(u, v, w)$, $z = \psi(u, v, w)$, then one has

$$\left(\frac{\partial x'}{\partial x}\right)_{y,z} = \frac{\begin{vmatrix} \frac{\partial x'}{\partial u} & \frac{\partial x'}{\partial v} & \frac{\partial x'}{\partial w} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \\ \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \end{vmatrix}}{\begin{vmatrix} \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} & \frac{\partial x}{\partial w} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \\ \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \end{vmatrix}} = \frac{\dfrac{\partial(x', y, z)}{\partial(u, v, w)}}{\dfrac{\partial(x, y, z)}{\partial(u, v, w)}}, \qquad \text{(II-35)}$$

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[15] A proof of this theorem for the case of functions of three independent variables is given in Appendix C to Part II.

provided all the partial derivatives in the determinants are continuous and provided the determinant in the denominator is not equal to zero.

In Tables II-1 to II-15 the values of the Jacobians are given for each set of three of the variables, T, p, M, V, U, S, as x, y, z, or x, y, z, and with T, p, M, as u, v, w. There are sixty Jacobians in the Table, but one has

$$\frac{\partial(x, y, z)}{\partial(u, v, w)} = -\frac{\partial(z, y, x)}{\partial(u, v, w)} = \frac{\partial(y, z, x)}{\partial(u, v, w)} \qquad \text{(II-36), (II-37)}$$

because interchanging two rows of a determinant changes the sign of the determinant. Hence it is only necessary to calculate the values of twenty of the sixty Jacobians. The calculations of these twenty Jacobians follow:

$$\frac{\partial(M, T, p)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial M} \end{vmatrix} = 1 ; \qquad \text{(II-38)}$$

$$\frac{\partial(V, T, p)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial M} \end{vmatrix} = \left(\frac{\partial V}{\partial M}\right)_{T,p} = \breve{V} ; \qquad \text{(II-39)}$$

$$\frac{\partial(U, T, p)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial M} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial M} \end{vmatrix} = \left(\frac{\partial U}{\partial M}\right)_{T,p} = \breve{U}\,; \qquad \text{(II-40)}$$

$$\frac{\partial(S, T, p)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial M} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial M} \end{vmatrix} = \left(\frac{\partial S}{\partial M}\right)_{T,p} = \breve{S}\,; \qquad \text{(II-41)}$$

$$\frac{\partial(V, T, M)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \end{vmatrix} = -M\left(\frac{\partial \breve{V}}{\partial p}\right)_{T}\,; \qquad \text{(II-42)}$$

$$\frac{\partial(U, T, M)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial M} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \end{vmatrix} = M\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p} + p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T}\right]; \qquad \text{(II-43)}$$

$$\frac{\partial(S,T,M)}{\partial(T,p,M)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial M} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \end{vmatrix} = M\left(\frac{\partial \breve{V}}{\partial T}\right)_p ; \qquad \text{(II-44)}$$

$$\frac{\partial(U,T,V)}{\partial(T,p,M)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial M} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \end{vmatrix} = M\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{V}}{\partial p}\right)_T + \breve{V}T\left(\frac{\partial \breve{V}}{\partial T}\right)\right] ; \qquad \text{(II-45)}$$

$$\frac{\partial(S,T,V)}{\partial(T,p,M)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial M} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \end{vmatrix} = M\left[\breve{V}\left(\frac{\partial \breve{V}}{\partial T}\right)_p + \breve{S}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right] ; \qquad \text{(II-46)}$$

$$\frac{\partial(S,T,U)}{\partial(T,p,M)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial M} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial M} \end{vmatrix} = M\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial T}\right)_p - \breve{S}p\left(\frac{\partial \breve{V}}{\partial p}\right)\right] ; \qquad \text{(II-47)}$$

$$\frac{\partial(V, p, M)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial M} \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \end{vmatrix} = M\left(\frac{\partial \breve{V}}{\partial T}\right)_p ; \tag{11-48}$$

$$\frac{\partial(U, p, M)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial M} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial M} \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \end{vmatrix} = M\left[\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right] ; \tag{11-49}$$

$$\frac{\partial(S, p, M)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial M} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial M} \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \end{vmatrix} = M\,\frac{\breve{c}_p}{T} ; \tag{11-50}$$

$$\frac{\partial(U, p, V)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial M} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial M} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \end{vmatrix} = -M\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{V}}{\partial T}\right)_p - \breve{c}_p\breve{V}\right] ; \tag{11-51}$$

$$\frac{\partial(S,p,V)}{\partial(T,p,M)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial M} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial M} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \end{vmatrix} = M\left[\frac{\breve{c}_p}{T}\breve{V} - \breve{S}\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]; \tag{11-52}$$

$$\frac{\partial(S,p,U)}{\partial(T,p,M)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial M} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial M} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial M} \end{vmatrix} = M\left[\frac{\breve{c}_p}{T}(\breve{U} - T\breve{S}) + \breve{S}p\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]; \tag{11-53}$$

$$\frac{\partial(U,M,V)}{\partial(T,p,M)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial M} \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \end{vmatrix} = -M^2\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)_p + \breve{c}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]; \tag{11-54}$$

$$\frac{\partial(S,M,V)}{\partial(T,p,M)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial M} \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \end{vmatrix} = -M^2\left[\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]; \tag{11-55}$$

$$\frac{\partial(S, M, U)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial M} \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial M} \end{vmatrix} = M^2\left[p\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{p\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right] ; \tag{II-56}$$

$$\frac{\partial(S, V, U)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial M} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial M} \end{vmatrix}$$

$$= M^2\left\{\left[\breve{U} + p\breve{V} - T\breve{S}\right]\left[\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]\right\} . \tag{II-57}$$

Table II-1 Jacobians of extensive functions for a one-component system of one phase	
$\frac{\partial(x', y, z)}{d(T, p>M)}$, $\frac{30:, y, z)}{3(7\% p, tt)}$	
y, z / x' x	T, p
M	1
V	$\breve{V}$
U	V
S	$\breve{S}$

Table II-2
Jacobians of extensive functions for a one-component system of one phase

$$\frac{d(x', y, z)}{3(T, p, M)} \;{}^{f}\; \frac{d(x, y, z)}{3(T, p, M)}$$

y, z / x	T, M
P	-1
V	$-M\left(\frac{\partial \breve{V}}{\partial p}\right)_T$
U	«[r©p * '(111
S	$M\left(\frac{\partial \breve{V}}{\partial T}\right)_p$

Table II-3
Jacobians of extensive functions for a
one-component system of one phase

$$\frac{\partial(x', y, z)}{\partial(T, p, M)} * \frac{\partial(x, y, z)}{\partial(T, p, M)}$$

x' \ y, z (x)	T, V
p	$-\breve{V}$
M	$M\left(\frac{\partial \breve{V}}{\partial p}\right)_T$
U	$M\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{V}}{\partial p}\right)_T + \breve{V}T\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]$
S	$M\left[\breve{V}\left(\frac{\partial \breve{V}}{\partial T}\right)_p + \breve{S}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$

Table II-4
Jacobians of extensive functions for a
one-component system of one phase

$$\frac{\partial(W, y, z)}{\partial(T, p, M)} = \frac{\partial(x, y, z)}{\partial(T, p, M)}$$

y, z / x	T, U
p	$-\breve{U}$
M	$-M\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)_p + p\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$
V	$-M\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{V}}{\partial p}\right)_T + \breve{V}T\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]$
S	$M\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial T}\right)_p - \breve{S}p\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$

Table II-5
Jacobians of extensive functions for a
one-component system of one phase

$\frac{Hx'_f\ y,z)}{d(T,p,M)}$ ' $\frac{d(x_f y,z)}{d(T,p,M)}$

x' \ x	T, S
p	-S
M	·»$(i)_p$
V	$-M\left[\breve{V}\left(\frac{\partial\breve{V}}{\partial T}\right)_p + \breve{S}\left(\frac{\partial\breve{V}}{\partial p}\right)_T\right]$
U	$-M\left[(\breve{U} - T\breve{S})\left(\frac{\partial\breve{V}}{\partial T}\right)_p - \breve{S}p\left(\frac{\partial\breve{V}}{\partial p}\right)_T\right]$

Table II-6
Jacobians of extensive functions for a one-component system of one phase

$$\frac{\partial(x, y, z)}{\partial(T,p,M)}, \quad \frac{\partial(x, y, z)}{\partial(T,p,M)}$$

x \ y, z	p, M
T	1
V	$M\left(\frac{\partial \breve{V}}{\partial T}\right)_p$
U	$M\left[\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]$
S	$M\frac{\breve{c}_p}{T}$

Table II-7
Jacobians of extensive functions for a
one-component system of one phase

d(x', Yf z) / d(T,p,M) ' 3(x, y, z) / 3(T, p,M)

\Yt Z x'\ X	p;V
T	V
M	$-M\left(\frac{\partial V}{\partial T}\right)_p$
u	-M[CU * p?)(ff)p - ? /]
S	-[?»- S1I)J

Table II-8
Jacobians of extensive functions for a
one-component system of one phase

$$\frac{\partial(x, y, z)}{\partial(T, p, M)}, \quad \frac{\partial(x, y, z)}{\partial(T, p, M)}$$

x \ y, z	p, U
T	$\breve{U}$
M	$-M\left[\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]$
V	$M\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{V}}{\partial T}\right)_p - \breve{c}_p\breve{V}\right]$
S	$M\left[\frac{\breve{c}_p}{T}(\breve{U} - T\breve{S}) + \breve{S}p\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]$

Table II-9
Jacobians of extensive functions for a one-component system of one phase

$$\frac{\partial(x', y, z)}{\partial(T, p, M)}, \quad \frac{\partial(x, y, z)}{\partial(T, p, M)}$$

y, z / x', x	p, S
T	[illegible] S
H	$-M\frac{\breve{C}_p}{T}$
y	[illegible]
U	$-M\left[\frac{\breve{C}_p}{T}(\breve{U} - T\breve{S}) + \breve{S}p\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]$

Table 11-10
Jacobians of extensive functions for a
one-component system of one phase

$$\frac{\partial(x', y, z)}{\partial(T, p, M)}, \quad \frac{\partial(x, y, z)}{\partial(T, p, M)}$$

y, z / x', x	M, V
T	$-M\left(\frac{\partial \breve{V}}{\partial p}\right)_T$
P	$M\left(\frac{\partial \breve{V}}{\partial T}\right)_p$
U	$-M^2\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \breve{c}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$
S	$-M^2\left[\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$

Table II-11
Jacobians of extensive functions for a
one-component system of one phase

$$\frac{\partial(x,y,z)}{\partial(T,p,M)} = \frac{\partial(x,y,z)}{\partial(T,p,M)}$$

$x \backslash y, z$	M, U
T	[illegible]
P	$M\left[\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]$
V	$M^2\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \breve{c}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$
S	$M^2\left[p\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{p\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$

Table 11-12
Jacobians of extensive functions for a
one-component system of one phase

$$\frac{\partial(x', y, z)}{\partial(T, p, M)}, \quad \frac{\partial(x, y, z)}{\partial(T, p, M)}$$

$x' \backslash x$	M, S
T	$Jd\breve{V}\backslash$
P	$M\frac{\breve{c}_p}{T}$
V	$M^2\left[\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$
U	$-M^2\left[p\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{p\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$

Table 11-13
Jacobians of extensive functions for a one-component system of one phase

$\frac{3(x', y, z)}{3(T, p, Af.)}$ ' $\frac{3(x, y, z)}{3(T, p, Af)}$

y, z / $x' \backslash x$	7, U
T	$M\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{V}}{\partial p}\right)_T + \breve{V}T\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]$
P	$-M\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{V}}{\partial T}\right)_p - \breve{c}_p \breve{V}\right]$
X	$-M^2\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \breve{c}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$
S	$M^2\left\{\left[\breve{U} + p\breve{V} - T\breve{S}\right]\left[\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]\right\}$

Table 11-14
Jacobians of extensive functions for a one-component system of one phase

3(x't yfz) / a(r, p. M) ' 3(x, yt z) / a(T, p, A/)

\ y, z / x \	V, S
T	f(ĭ)/²(li]
P	$N\left[\frac{\breve{C}_p}{T}\breve{V} - \breve{S}\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]$
M	-[(H²)/*(li]
U	$-N^2\left\{\left[\breve{U} + p\breve{V} - T\breve{S}\right]\left[\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]\right\}$

Table 11-15
Jacobians of extensive functions for a one-component system of one phase

$$\frac{\partial(x', y, z)}{\partial(T, p, M)}, \quad \frac{\partial(x, y, z)}{\partial(T, p, M)}$$

y, z / x' / x	U, S
T	$M\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial T}\right)_p - \breve{S}p\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$
p	$M\left[\frac{\breve{C}_p}{T}(\breve{U} - T\breve{S}) + \breve{S}p\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]$
M	$M^2\left[p\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{p\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$
U	$M^2\left\{\left[\breve{U} + p\breve{V} - T\breve{S}\right]\left[\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]\right\}$

In order to obtain the first partial derivative of any-one of the six quantities, T, p, M, V, U, S with respect to any second quantity of the six when any third and fourth quantities of the six are held constant, one has only to divide the value of the Jacobian in which the first letter in the first line is the quantity being differentiated and in which the second and third letters in the first line are the quantities held constant by the value of the Jacobian in which the first letter of the first line is the quantity with respect to which the differentiation is taking place and in which the second and third letters in the first line are the quantities held constant.

To obtain the relation among any four derivatives having expressed them in terms of the same three derivatives, $\left(\frac{\partial V}{\partial T}\right)_p$, $\left(\frac{\partial V}{\partial p}\right)_T$, and C_p, one can then eliminate the three derivatives from the four equations, leaving a single equation connecting the four derivatives. In addition to the relations among four derivatives there are also degenerate cases in which there are relations among fewer than four derivatives.

In case a relation is needed that involves one or more of the thermodynamic potential functions, $H \equiv U + pV$, $A \equiv U - TS$, $G \equiv U + pV - TS$, partial derivatives involving one or more of these functions can also be calculated as the quotients of two Jacobians, which can themselves be calculated by the same method used to calculate the Jacobians in Tables II-1 to II-15.

It is interesting to note that in the transformations of the thermodynamic quantities T, p, M, V, U, S from one coordinate space based on any three of these six quantities to another coordinate space likewise based on three of these six quantities, the enthalpy H, the Helmholtz function A, and the Gibbs function G appear automatically in the expressions for many of the Jacobians involved.

Appendix A to Part II

Discussion of the definitions of heat and work in the case of open systems used by various authors

According to Larmor,[1] Morey,[2] Goranson,[3] Moelwyn-Hughes, ** Callen,[5] and Wheeler[6] in the case of an open system to which mass is added or from which mass is taken away, the differential of the heat received dQ is equal to the absolute thermodynamic temperature T times the differential of the entropy of the system dS. Neither Larmor nor Morey nor Goranson nor Moelwyn-Hughes nor Callen gave an operational analysis of any open system in support of their conclusion that $dQ = TdS$ in the case of open systems. Wheeler attempted to explain the Gibbs differential equation for an open system

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[1] Larmor, Sir Joseph, Proc. Roy. Soc. London, 75, 289-290, 1905.

[2] Morey, G.W., Jour. Franklin Inst., 194, 433-434, 1922.

[3] Goranson, R.W., *Thermodynamic Relations in Multi-Component Systems,* Carnegie Institution of Washington Publication No. 408, 1930, pp. 39, 41, 44, 52.

% Moelwyn-Hughes, E.A., *Physical Chemistry,* Pergamon Press, London, New York, Paris, 1957, p. 287.

[5] Callen, H.B., *Thermodynamics$* John Wiley and Sons, Inc., New York and London, 1960, p« 192.

[6] Wheeler, L.P., *Josiah Willard Gihbs-The History of a Great Mind,* Rev. Ed.f Yale University Press, Mew Haven, 1952, p. 76.

of n components

$$dU = TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2 \ldots + \mu_n dm_n,^{7}$$

where $\mu_1, \mu_2, \ldots \mu_n$ denote the chemical potentials of components 1, 2, ... n, and $m_1, m_2, \ldots m_n$ denote the masses of components 1, 2, ... n in the open system, in the following way. Wheeler supposed that an:

> . . . imaginary box is constructed with walls which in addition to being elastic and thermally conducting are also porous, so that the solution can pass freely through the pores in either direction - from inside out or from outside in. Then if the condition of the fluid is slightly altered as before, the change in energy in the box will depend not only on the heat which may enter or leave and the volume change due to the buckling of the walls but also on the masses of the components of the fluid going through the pores. Thus this energy change cannot be computed by the prime equation[8] as it stands. It must be altered by the addition of as many energy terms as there are components of the fluid passing through the walls. If there are n such components, the generalized prime equation will express the change in energy in terms of *n* + 2 independent variables. Each of the added

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[7] Gibbs, J. Willard, Trans. Conn. Acad. of Arts and Sciences, 3, 116, 1874-78, or *Collected Works,* Longmans, Green and Co., New York, 1928, **Vol.** 1, p. 63.

[8] The equation here referred to as the prime equation is the Clausius differential equation for closed systems:

$$dU = TdS - pdV.$$

> energy terms, in analogy to those in the prime equation, Gibbs expresses as the product of two factors, one an intensity and the other an extension factor. Thus just as the heat term is expressed as the product of temperature and the change in entropy, and the work term as the product of pressure and the change in volume, so an energy term due to the added mass of any component was expressed as the product of what Gibbs termed a "potential" and the change in mass.

However, according to Gillespie and Coe[9] in the case of an open system

$$dS = \frac{dQ}{T} + \sum_i \breve{S}_i dm_i \qquad \text{(II-A-1)}$$

when there is simultaneous reversible transfer of both heat and mass. In this equation, *dS* denotes the increase in the entropy of the open system, *dQ* the amount of heat received by the open system, *T* the absolute thermodynamic temperature of the open system, $\breve{S}_i$ the entropy of unit mass of kind i added to the open system, and dm_i the mass of kind i added to the open system.

The equation of Gillespie and Coe applied to the case of an open system in which there is simultaneous reversible transfer of both heat and mass appears to be correct. Let us consider the following simplest imaginable case of an open system. In a thermostat filled with water, suppose that one has a cylinder closed at both ends by pistons and containing a

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[9] Gillespie, L.J., and J.E. Coe, Jr., Jour. Chem. Phys., 1, 105, 1933.

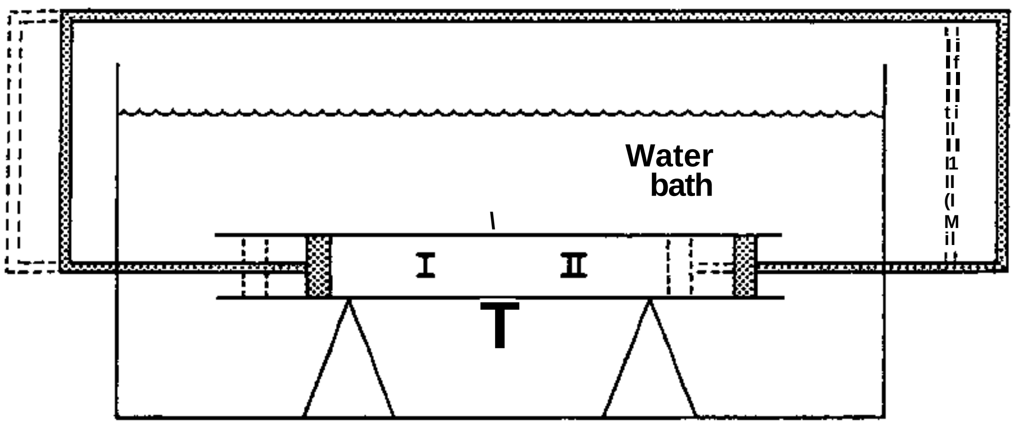

Figure II-A-1

fluid of constant composition (Figure II-A-1). Suppose further that the pistons are connected by a rigid bar so that the volume between them remains constant. In Figure II-A-1, let the two arrows indicate the position of a fixed circular line around the cylinder. The fluid between the two pistons constitutes a closed system and at this stage the temperature, pressure, and volume of the total mass of fluid are kept constant. Let us next suppose that the two pistons are moved slowly to the left in unison from the positions indicated in Figure II-A-1 by solid lines to the positions indicated by dotted lines. The mass of fluid to the left of the arrows then has received an addition and that to the right of the arrows has undergone a diminution. The mass of fluid to the left of the arrows has constituted an open system which we designate as system I. Likewise, the mass of fluid to the right of the arrows has constituted a second open system which we designate as system II. Systems I and II together make up a closed system, the entropy of which has remained constant. The entropy of system I, S^I, has increased by an amount equal to the specific entropy of the fluid times the mass of the fluid that has been moved past the arrows from right to left and the entropy of system II, S^{II}, has decreased by the same amount. Thus, we had:

$$dS^I = \breve{S}dM^I, \qquad \text{(II-A-2)}$$

$$dS^{II} = \breve{S}dM^{II} = -\breve{S}dM^I; \qquad \text{(II-A-3)(II-A-4)}$$

and

$$dS^I + dS^{II} = 0, \qquad \text{(II-A-5)}$$

where $\breve{S}$ denotes the specific entropy of the fluid and M^I and

A/II denote the masses of systems I and II. At the same time, no heat has been received by the fluid from the water bath since the temperature of the fluid has remained the same as that of the water bath and the pressure and total volume of the fluid have remained constant. The question then remains to be answered whether or not it can be said that system I has received any heat and similarly whether or not system II has given up any heat. To say that at constant temperature, constant pressure, and constant specific volume *x* grams of fluid have transported y calories of heat from system II to system I is the same as saying that these *x* grams of fluid at the constant temperature t' and constant pressure p' contained y calories of heat which they carried with them. It is well known in calorimetry, thermodynamics, and statistical mechanics that it is not possible to say that a body at a certain temperature and pressure contains a certain amount of heat* Doolittle and Zerban[10] have stated that "most modern authors of texts on thermodynamics and on physics have agreed on the following conception of heat: Heat is energy transferred from one substance to another substance because of a temperature difference between the two substances." In the case we have been discussing, system I, system II, and the water bath of the thermostat have all remained at the same temperature. Consequently, it cannot be said that there has been any heat flow from the water bath to system I or system II or from system II to system I. At constant temperature, constant pressure, and constant specific volume, we thus had:

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[10] Doolittle, J.S., and **A.H. Zerban,** *Engineering Thermodynamics,* International Textbook Co., Scranton, 1948, p. 8.

$$dQ^{I} = 0, \qquad \text{(II-A-6)}$$

$$dQ^{II} = 0, \qquad \text{(II-A-7)}$$

and

$$dQ^{I} + dQ^{II} = 0, \qquad \text{(II-A-8)}$$

where Q^{I} and Q^{II} denote the heat quantities received by systems I and II. Thus the heat received by a one-component system of one phase and of variable mass can be represented by the line integral

$$Q = \int^{T,\,p,\,M} [M c_p dT + M l_p dp + 0\, dM] \qquad \text{(II-A-9)}$$ [11]

where c_p and l_p are functions of T and p and the coefficient of dM is zero.

We turn next to the question of the definition of work in the case of a one-component system of one phase and of variable mass. In this case it remains to be determined whether or not dW is equal to pdV if one wishes to introduce a definition of work in the case of an open system when mass is being transferred to or from the system. Several authors,

[11] The question of the definition of the heat received by a one-conponent system of one phase and of variable mass has been discussed by this author more comprehensively on pages 17 to 33 of Carnegie Institution of Washington Publication No. 408A entitled *Thermodynamic Relations in Open Systems* published in 1977.

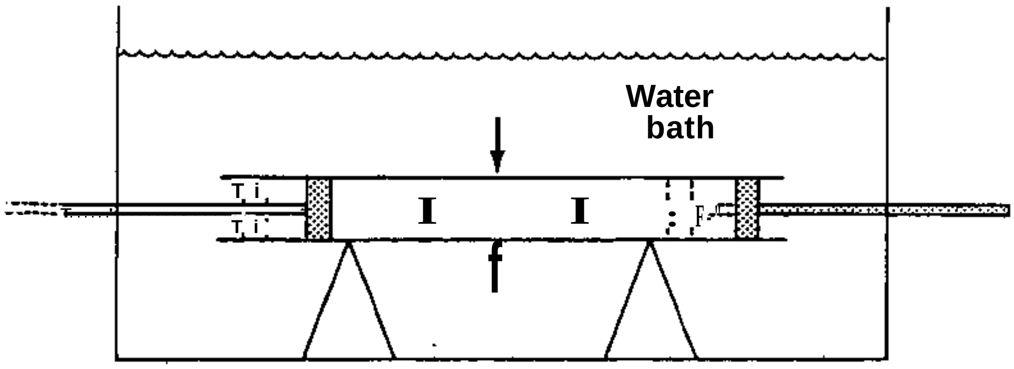

Figure II-A-2

Morey,[12] Goranson,[13] Moelwyn-Hughes,[14] and Wheeler,[15] have stated that in the GIbbs differential equation $dW = pdV$. However, none of these authors drew a diagram of an open system and none of them apparently realized that this statement does not carry over from the Clausius differential equation for a closed system without the necessity of an important new physical decision.

In regard to the question of the definition of work in the case of an open system, we may note that G.J. Van Wylen,[16] formerly Chairman of the Department of Mechanical Engineering at the University of Michigan, states in his book entitled *Thermodynamics* that "A final point should be made regarding the work done by an open system: Matter crosses the boundary of the system, and in so doing, a certain amount of energy crosses the boundary of the system. Our definition of work does not include this energy."

The question of the definition of work in the case of an open system has been discussed by the present author with Professor R.L. Wild of the Physics Department at the University of California at Riverside. In this discussion we supposed that in a thermostat filled with water there was a cylinder closed at both ends by pistons and containing a fluid of constant composition (Figure II-A-2). In Figure II-A-2

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[12] Morey, G.V., op. cit., p. 434.

[13] Goranson, R.W., op. cit., pp. 39, 44.

[14] Moelwyn-Hughes, E.A., op. cit., p. 287.

[15] Wheeler, L.P., op. cit., p. 76.

[16] Van Wylen, G.J., *Thermodynamics,* John Wiley and Sons, Inc., New York, 1959, p. 49.

the two arrows indicated the position of a fixed circular line around the cylinder. The fluid between the two pistons constituted a closed system and at this stage the temperature, pressure, and volume of the total mass of fluid were kept constant. We next supposed that the two pistons were moved slowly to the left in unison from the positions indicated in Figure II-A-2 by solid lines to the positions indicated by dotted lines. The mass of fluid to the left of the arrows then had received an addition and that to the right of the arrows had undergone a diminution. The mass of fluid to the left of the arrows constituted an open system which we designated as system I. Likewise, the mass of fluid to the right of the arrows constituted a second open system which we designated as system II. Systems I and II together made up a closed system, the energy of which remained constant. The energy of system I, U^I, had increased by an amount equal to the specific energy of the fluid times the mass of the fluid that had been moved past the arrows from right to left, and the energy of system II, U^{II}, had decreased by the same amount. Thus we had

$$dU^I = \breve{U} dM^I, \qquad \text{(II-A-10)}$$

$$dU^{II} = \breve{U} dM^{II} = -\breve{U} dM^I, \qquad \text{(II-A-11)(II-A-12)}$$

and

$$dU^I + dU^{II} = 0, \qquad \text{(II-A-13)}$$

where $\breve{U}$ denotes the specific energy of the fluid, and M^I and M^{II} denote the masses of open systems I and II. In the case of the open one-component system, system I, work was certainly done by the fluid on the piston at the left hand end equal to the pressure times the increase in volume

$$dW^{I} = p\breve{V}dM^{I}, \qquad \text{(II-A-14)}$$

where p denotes the pressure of the fluid, and V denotes the specific volume of the fluid. Since the change in energy of system I was $\breve{U}dM^{I}$ and work was done by system I equal to $p\breve{V}dM^{I}$, the amount of energy that came across the fixed boundary with the incoming mass was $\breve{U}dM^{I} + p\breve{V}dM^{I}$ which was equal to $\breve{H}dM^{I}$. According to Van Wylen[17] none of the energy represented by the term $\breve{H}dM^{I}$ is to be considered as work and this was confirmed by Professor Wild. Thus we had

$$dU^{I} = \breve{H}dM^{I} - dW^{I}, \qquad \text{(II-A-15)}$$ [18]

The major new physical decision that has to be made if the definition of work is to be extended from the case of a closed system to the case of an open system is whether or not it can be said that work is done at a fixed boundary surface across which mass is transported. Van Wylen and Professor Wild have concluded that it cannot be said that work is done at a fixed boundary surface across which mass is transported.

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[17] fan Wylen, op. cit., pp. 49, 75-77, 80.

[18] Hall and Ibele in their treatise entitled *Engineering Thermodynamics* (Prentice-Kail, Inc., Englewood Cliffs, N,J., 1960) stated on page 108 that "A general equation for energy change in an open system can be written

$$dE = dQ - dW + \sum_i (e + pv)_i dm_i. \qquad (7.25)"$$

This equation reduces to equation (II-A-15) in the case of a transfer of mass of constant composition at constant temperature and constant pressure, in which case $dQ = 0$.

Sage,[19] on the other hand, stated that in the case of an system of constant composition if the material added to ;ystem is at the same pressure as that of the system the litesimal amount of work w is given by the equation

$$w + j = pdV - p\breve{V}dm. \tag{3.18}$$

lis equation j represents frictional work (which would :e to zero in a reversible change). Sage[20] stated further- an open system is one for which material is transported JS the boundaries. Sage's equation (3.18) is thus ided to be applicable to open system I of Figure II-A-2, lis case V is a function of T, p, and m and

$$dV = \frac{\partial V}{\partial T}dT + \frac{\partial V}{\partial p}dp + \frac{\partial V}{\partial m}dm \tag{II-A-16}$$

furthermore

$$\frac{V}{m} = \breve{V} . \tag{II-A-17}$$

according to Sage

$$w + j = p\frac{\partial V}{\partial T}dT + p\frac{\partial V}{\partial p}dp + p\breve{V}dm - p\breve{V}dm$$

$$= p\frac{\partial V}{\partial T}dT + p\frac{\partial V}{\partial p}dp . \tag{XI-A-18}$$

:he transfer of material of constant composition is at

Sage, B.H., *Thermodynamics of Multicomponent Systems,* ihold Publishing Corp., New York, 1965, p. 47.

Sage, B.H., op. cit., p. 46.

constant temperature and constant pressure according to Sage $w + j = 0$. Thus in the case of open system I discussed on page 82 according to Sage $w + j = 0$, Since open system I for certain performed work $p\breve{V}dM^\wedge$ against the enclosing piston Sage's conclusion requires that the $p\breve{V}dM^\wedge$ part of the $\breve{H}dM^\wedge$ term be considered as work offsetting the work done by open system I against the enclosing piston. In other words, Sage[21] considers part of the energy associated with the mass transferred across the fixed boundary to be work, contrary to the conclusion of Van Wylen, Goranson, and Professor Wild. The decision between these conflicting views is one to be made by physicists and engineers and is, I believe, of some interest, but so far as I am aware, all of the thermodynamic relations and measurements needed in physical chemistry can be obtained without involving any such decision or any definition of work in the case of an open system.[22]

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[21] Sage (op. cit., p. 47) stated that "This definition of work for a constant-composition system of variable weight differs markedly from that used by Gibbs and Goranson." According to Sage, work is defined by these authors for cases in which j is zero as follows:

$$w = pdV = mp\left[\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,m} dT + \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,m} dp\right] + p\breve{V}dm .$$

This statement is correct as far as Goranson is concerned, but in regard to Gibbs it is not correct, since Gibbs nowhere mentioned work or heat in connection with an open system in his memoir entitled "On the Equilibrium of Heterogeneous Substances."

[22] The definition of work in the case of open systems has been of interest chiefly to engineers concerned with flow processes (see, for example, J. H. Keenan, *Thermodynamics,* John Wiley and Sons, Inc., New York, 1948, p. 35).

In accordance with the conclusion of Van Wylen, Goranson, and Professor Wild, the work W done by a one-component system of one phase and of variable mass can thus be represented by the line integral

$$W = \int_{T_0, p_0, M_0}^{T, p, M} \left\{ M p \left(\frac{\partial \breve{V}}{\partial T}\right)_p dT + M p \left(\frac{\partial \breve{V}}{\partial p}\right)_T dp + p \breve{V} dM \right\}. \qquad \text{(II-A-19)}$$

This equation for work in the case of an open one-component system of one phase or the corresponding differential form

$$dW = p\left(\frac{\partial V}{\partial T}\right)_p dT + p\left(\frac{\partial V}{\partial p}\right)_T dp + p\breve{V} dM , \qquad \text{(II-A-20)}$$

has been found to be of use in some engineering problems.

Appendix B to Part II

Transformation of the work and heat line integrals from one coordinate space to other coordinate spaces in the case of a one-component system of one phase and of variable mass

In Part II it was shown that it is not necessary to define either work or heat in the case of an open system of one component and of one phase when mass is being transferred to or from the system in order to obtain the energy and the entropy as functions of the absolute thermodynamic temperature, the pressure, and the total mass from experimental measurements. Thus the derivation of the Jacobians listed in Tables II-l to 11-15 did not depend upon definitions of work or heat in the case of an open system of one component and of one phase when mass is being transferred to or from the system.

For some purposes, however, it is useful to have definitions of work and heat in the case of an open system of one component and of one phase when mass is being transferred to or from the system as was shown in Appendix A to Part II. The derivatives of the work done by a system of one component and one phase and of variable mass are total derivatives with respect to the variables chosen as the parameters defining the paths of the integral. In order to obtain the total derivative of the work done along a straight line parallel to one of the coordinate axes in any coordinate space one obtains from Tables II-l to 11-15 the partial derivative of the volume with respect to the quantity plotted along that axis when the quantitites plotted along the other axes are held .constant and one multiplies this partial derivative by the pressure.

The derivatives of the heat received by a system of one component and one phase and of variable mass are also total derivatives with respect to the variables chosen as the parameters defining the paths of the integral. However, the derivatives of the heat received by a one-component system of one phase and of variable mass along straight lines parallel to the coordinate axes in various coordinate spaces cannot be obtained by multiplication of the' partial derivatives of the entropy by the absolute thermodynamic temperature when transfer of masses to or from the system are involved. In such cases the total derivatives of the heat received along lines parallel to the coordinate axes in any desired coordinate space can be derived in terns of the total derivatives of the heat received along lines parallel to the coordinate axes in (7\ p, A/)-space by transformation of the heat line integrals as explained in the second half of Appendix C to Part II. Following is an example of such a transformation. In the case of a one-component system of one phase and of variable mass the heat line integral extended along a path in (7\ M* F)-space is

$$Q = \int_{T_0, M_0, V_0}^{T, M, V} \left\{ \frac{dQ}{dT} dT + \frac{dQ}{dM} dM + \frac{dQ}{dV} dV \right\}$$

$$= \int^{T, M, V} \left\{ M \check{c}_V dT + \frac{dQ}{dN} dM + l_V dV \right\} . \qquad \text{(II-B-1)}$$

In order to transform this integral to (T, p, M)-space we make use of equations (II-C-63), (II-C-64), and (II-C-65) in Appendix C to Part II. For the purpose of substitution of values in equations (II-C-63), (II-C-64) and (II-C-65) the equivalence of symbols is given in the following Table.

Table II-B-1

Equivalence of symbols

Γ	Q
x	T
y	M
z	V
$\left(\frac{\partial \Gamma}{\partial x}\right)_{y,z}$	$\left(\frac{\partial Q}{\partial T}\right)_{M,V}$
$\left(\frac{\partial \Gamma}{\partial y}\right)_{x,z}$	$\left(\frac{\partial Q}{\partial M}\right)_{T,V}$
$\left(\frac{\partial \Gamma}{\partial z}\right)_{x,y}$	$\left(\frac{\partial Q}{\partial V}\right)_{T,M}$
u	T
v	p
w	M
$\left(\frac{\partial \Gamma}{\partial u}\right)_{v,w}$	MC_p
$\left(\frac{\partial \Gamma}{\partial v}\right)_{u,w}$	Ml_p
$\left(\frac{\partial \Gamma}{\partial w}\right)_{u,v}$	0

Substituting the values from Table II-B-1 in equation (II-C-63) we have

$$\left(\frac{dQ}{dT}\right)_{M,V} = M\breve{c}_V = \frac{\begin{vmatrix} M\breve{c}_p & M\breve{L}_p & 0 \\ \frac{dM}{dT} & \frac{dM}{dp} & \frac{dM}{dM} \\ \frac{dV}{dT} & \frac{dV}{dp} & \frac{dV}{dM} \end{vmatrix}}{\begin{vmatrix} \frac{dT}{dT} & \frac{dT}{dp} & \frac{dT}{dM} \\ \frac{dM}{dT} & \frac{dM}{dp} & \frac{dM}{dM} \\ \frac{dV}{dT} & \frac{dV}{dp} & \frac{dV}{dM} \end{vmatrix}}, \qquad \text{(II-B-2)}$$

and multiplying out the quantities in the determinants we obtain

$$\left(\frac{dQ}{dT}\right)_{M,V} = M\breve{c}_V = \left[M\breve{\ } \; dv \; {}_M\wedge \; dvi. \; r \; dv \right]$$

Jw fdv̆\ J̆dvVl ./d̆v\ (II-3-3)
\op /$_T$ \o /$_p$ \op>'T'

Similarly, substituting the values from Table II-3-1 in equation (II-C-64) we have

$$\left(\frac{dQ}{dM}\right)_{T,V} = \frac{\begin{vmatrix} M\breve{c}_p & M\breve{l}_p & 0 \\ \frac{dT}{dT} & \frac{dT}{dp} & \frac{dT}{dM} \\ \frac{dV}{dT} & \frac{dV}{dp} & \frac{dV}{dM} \end{vmatrix}}{\begin{vmatrix} \frac{dM}{dT} & \frac{dM}{dp} & \frac{dM}{dM} \\ \frac{dT}{dT} & \frac{dT}{dp} & \frac{dT}{dM} \\ \frac{dV}{dT} & \frac{dV}{dp} & \frac{dV}{dM} \end{vmatrix}} , \qquad \text{(II-B-4)}$$

and multiplying out the quantities in the determinants we obtain

$$\left(\frac{dQ}{dM}\right)_{T,V} = \left[-\breve{l}_p \frac{\partial V}{\partial M}\right] \div \left[\frac{\partial V}{\partial p}\right]$$

$$= \left[T\breve{V}\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right] \div \left(\frac{\partial \breve{V}}{\partial p}\right)_T . \qquad \text{(II-B-5)}$$

Finally, substituting the values from Table II-B-1 in equation (II-C-65) we have

$$\left(\frac{\partial Q}{\partial V}\right)_{T,M} = l_v = \frac{\begin{vmatrix} M\breve{c}_p & M\breve{l}_p & 0 \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \end{vmatrix}}{\begin{vmatrix} \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \end{vmatrix}}, \qquad \text{(II-B-6)}$$

and multiplying out the quantities in the determinants we obtain

$$\left(\frac{\partial Q}{\partial V}\right)_{T,M} = l_v = \left[-M\breve{l}_p\right] \div \left[-\frac{\partial V}{\partial p}\right]$$

$$= \left[-T\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right] \div \left(\frac{\partial \breve{V}}{\partial p}\right)_T, \qquad \text{(II-B-7)}$$

The corresponding values of the partial derivatives of the entropy obtained from Tables 11-10, II-3, and II-2 are

$$\left(\frac{\partial S}{\partial T}\right)_{p} = \left[\frac{\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\ldots}\right) \ldots \left(\frac{\partial \breve{V}}{\ldots}\right)^2_{p}\right] \div \left(\frac{\partial \breve{V}}{\ldots}\right)_T \qquad \text{(II-B-8)}$$

$$\left(\frac{\partial S}{\partial M}\right)_{T} = \left[\breve{V}\left(\frac{\partial \breve{V}}{\partial T}\right)_p + \breve{S}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right] \div \left(\frac{\partial \breve{V}}{\partial p}\right)_T , \qquad \text{(II-B-9)}$$

and

$$\left(\frac{\partial S}{\partial V}\right)_{T, M} = \left[-\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right] \div \left(\frac{\partial \breve{V}}{\partial p}\right)_T . \qquad \text{(II-B-10)}$$

Thus it follows from (XI-B-3), (II-B-7), (II-B-8), and (II-B-10) that

$$\left(\frac{dQ}{dT}\right)_{M, V} = T\left(\frac{\partial S}{\partial T}\right)_{M, V} \qquad \text{(II-B-11)}$$

and

$$\left(\frac{dQ}{dV}\right)_{T, M} = T\left(\frac{\partial S}{\partial V}\right)_{T, M} , \qquad \text{(II-B-12)}$$

but, finally, it also follows from (II-B-5) and (II-B-9) that

$$\left(\frac{dQ}{dM}\right)_{T, V} = T\left(\frac{\partial S}{\partial M}\right)_{T, V} \qquad \text{(II-B-13)}$$

Proofs of the relations:

$$\left(\frac{\partial x'}{\partial x}\right)_{y,z} = \frac{\dfrac{\partial(x', y, z)}{\partial(u, v, w)}}{\dfrac{\partial(x, y, z)}{\partial(u, v, w)}}$$

and

$$\left(\frac{\partial x'}{\partial x}\right)_{y,z} = \frac{\begin{vmatrix} \frac{\partial x'}{\partial u} & \frac{\partial x'}{\partial v} & \frac{\partial x'}{\partial w} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \\ \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \end{vmatrix}}{\begin{vmatrix} \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} & \frac{\partial x}{\partial w} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \\ \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \end{vmatrix}}$$

It is assumed that x' is a function of x, y, and z

$$x' = \psi(x, y, z). \qquad \text{(II-C-1)}$$

and that x, y, and z are functions of u, v, and w

$$x = f(u, v, w), \qquad \text{(II-C-2)}$$
$$y = \phi(u, v, w), \qquad \text{(II-C-3)}$$
$$z = \chi(u, v, w). \qquad \text{(II-C-4)}$$

It is assumed further that these functions are continuous together with their first partial derivatives. By application of the theorem for change of variables in partial differentiation one then obtains

$$\frac{\partial x'}{\partial u} = \frac{\partial x'}{\partial x}\frac{\partial x}{\partial u} + \frac{\partial x'}{\partial y}\frac{\partial y}{\partial u} + \frac{\partial x'}{\partial z}\frac{\partial z}{\partial u} , \qquad \text{(II-C-5)}$$

$$\frac{\partial x'}{\partial v} = \frac{\partial x'}{\partial x}\frac{\partial x}{\partial v} + \frac{\partial x'}{\partial y}\frac{\partial y}{\partial v} + \frac{\partial x'}{\partial z}\frac{\partial z}{\partial v} , \qquad \text{(II-C-6)}$$

and

$$\frac{\partial x'}{\partial w} = \frac{\partial x'}{\partial x}\frac{\partial x}{\partial w} + \frac{\partial x'}{\partial y}\frac{\partial y}{\partial w} + \frac{\partial x'}{\partial z}\frac{\partial z}{\partial w} . \qquad \text{(II-C-7)}$$

From equations (II-C-5), (II-C-6) and (II-C-7) it follows that

$$\frac{\partial x'}{\partial z}\frac{\partial z}{\partial u} = -\frac{\partial x'}{\partial x}\frac{\partial x}{\partial u} - \frac{\partial x'}{\partial y}\frac{\partial y}{\partial u} + \frac{\partial x'}{\partial u} , \qquad \text{(II-C-8)}$$

$$\frac{\partial x'}{\partial z}\frac{\partial z}{\partial v} = -\frac{\partial x'}{\partial x}\frac{\partial x}{\partial v} - \frac{\partial x'}{\partial y}\frac{\partial y}{\partial v} + \frac{\partial x'}{\partial v} \qquad \text{(II-C-9)}$$

and

$$\frac{\partial x'}{\partial z}\frac{\partial z}{\partial w} = -\frac{\partial x'}{\partial x}\frac{\partial x}{\partial w} - \frac{\partial x'}{\partial y}\frac{\partial y}{\partial w} + \frac{\partial x'}{\partial w} . \qquad \text{(II-C-10)}$$

Dividing both sides of equation (II-C-8) by $\frac{\partial z}{\partial u}$, and both sides of equation (II-C-9) by $\frac{\partial z}{\partial v}$, likewise both sides of equation (II-C-10) by Jl£ / ∂w we have

$$\frac{\partial x'}{\partial z} = \frac{\dfrac{\partial x'}{\partial u} - \dfrac{\partial x'}{\partial x}\dfrac{\partial x}{\partial u} - \dfrac{\partial x'}{\partial y}\dfrac{\partial y}{\partial u}}{\dfrac{\partial z}{\partial u}}, \tag{II-C-11}$$

$$\frac{\partial x'}{\partial z} = \frac{\dfrac{\partial x'}{\partial v} - \dfrac{\partial x'}{\partial x}\dfrac{\partial x}{\partial v} - \dfrac{\partial x'}{\partial y}\dfrac{\partial y}{\partial v}}{\dfrac{\partial z}{\partial v}}, \tag{II-C-12}$$

and

$$\frac{\partial x'}{\partial z} = \frac{\dfrac{\partial x'}{\partial w} - \dfrac{\partial x'}{\partial x}\dfrac{\partial x}{\partial w} - \dfrac{\partial x'}{\partial y}\dfrac{\partial y}{\partial w}}{\dfrac{\partial z}{\partial w}}. \tag{H-C-13}$$

It follov/s that the right side of equation (II-C-11) is equal to the right side of equation (II-C-12)

$$\frac{\dfrac{\partial x'}{\partial u} - \dfrac{\partial x'}{\partial x}\dfrac{\partial x}{\partial u} - \dfrac{\partial x'}{\partial y}\dfrac{\partial y}{\partial u}}{\dfrac{\partial z}{\partial u}} = \frac{\dfrac{\partial x'}{\partial v} - \dfrac{\partial x'}{\partial x}\dfrac{\partial x}{\partial v} - \dfrac{\partial x'}{\partial y}\dfrac{\partial y}{\partial v}}{\dfrac{\partial z}{\partial v}}. \tag{II-C-14}$$

Multiplying both sides of equation (II-C-14) by $\left(\frac{\partial z}{\partial v}\frac{\partial z}{\partial u}\right)$ we have

$$\frac{\partial z}{\partial v}\left(\frac{\partial x'}{\partial u} - \frac{\partial x'}{\partial x}\frac{\partial x}{\partial u} - \frac{\partial x'}{\partial y}\frac{\partial y}{\partial u}\right) = \frac{\partial z}{\partial u}\left(\frac{\partial x'}{\partial v} - \frac{\partial x'}{\partial x}\frac{\partial x}{\partial v} - \frac{\partial x'}{\partial y}\frac{\partial y}{\partial v}\right) \cdot \quad \text{(II-C-15)}$$

Likewise it follows that the right side of equation (II-C-12) is equal to the right side of equation (II-C-13)

$$\frac{\dfrac{\partial x'}{\partial v} - \dfrac{\partial x'}{\partial x}\dfrac{\partial x}{\partial v} - \dfrac{\partial x'}{\partial y}\dfrac{\partial y}{\partial v}}{\dfrac{\partial z}{\partial v}} = \frac{\dfrac{\partial x'}{\partial w} - \dfrac{\partial x'}{\partial x}\dfrac{\partial x}{\partial w} - \dfrac{\partial x'}{\partial y}\dfrac{\partial y}{\partial w}}{\dfrac{\partial z}{\partial w}} \cdot \quad \text{(II-C-16)}$$

Multiplying both sides of equation (II-C-16) by $\left(\frac{\partial z}{\partial v}\frac{\partial z}{\partial w}\right)$ we have

$$\frac{\partial z}{\partial w}\left(\frac{\partial x'}{\partial v} - \frac{\partial x'}{\partial x}\frac{\partial x}{\partial v} - \frac{\partial x'}{\partial y}\frac{\partial y}{\partial v}\right) = \frac{\partial z}{\partial v}\left(\frac{\partial x'}{\partial w} - \frac{\partial x'}{\partial x}\frac{\partial x}{\partial w} - \frac{\partial x'}{\partial y}\frac{\partial y}{\partial w}\right) \cdot \quad \text{(II-C-17)}$$

Consequently ve have from equations (II-C-15) and (II-C-17)

$$\frac{\partial z}{\partial v}\frac{\partial x'}{\partial u} - \frac{\partial z}{\partial v}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial u} - \frac{\partial z}{\partial v}\frac{\partial x'}{\partial y}\frac{\partial y}{\partial u} = \frac{\partial z}{\partial u}\frac{\partial x'}{\partial v} - \frac{\partial z}{\partial u}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial v} - \frac{\partial z}{\partial u}\frac{\partial x'}{\partial y}\frac{\partial y}{\partial v} \quad \text{(II-C-18)}$$

and

$$\frac{\partial z}{\partial w}\frac{\partial x'}{\partial v} - \frac{\partial z}{\partial w}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial v} - \frac{\partial z}{\partial w}\frac{\partial x'}{\partial y}\frac{\partial y}{\partial v} = \frac{\partial z}{\partial v}\frac{\partial x'}{\partial w} - \frac{\partial z}{\partial v}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial w} - \frac{\partial z}{\partial v}\frac{\partial x'}{\partial y}\frac{\partial y}{\partial w} \cdot \quad \text{(II-C-19)}$$

From equation (II-C-18) it follows that

$$\frac{\partial x'}{\partial y}\frac{\partial z}{\partial u}\frac{\partial y}{\partial v} - \frac{\partial x'}{\partial y}\frac{\partial z}{\partial v}\frac{\partial y}{\partial u} = \frac{\partial z}{\partial u}\frac{\partial x'}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial x'}{\partial u} + \frac{\partial z}{\partial v}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial u} - \frac{\partial z}{\partial u}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial v} \tag{II-C-20}$$

and from equation (II-C-19) it follows that

$$\frac{\partial x'}{\partial y}\frac{\partial z}{\partial v}\frac{\partial y}{\partial w} - \frac{\partial x'}{\partial y}\frac{\partial z}{\partial w}\frac{\partial y}{\partial v} = \frac{\partial z}{\partial v}\frac{\partial x'}{\partial w} - \frac{\partial z}{\partial w}\frac{\partial x'}{\partial v} + \frac{\partial z}{\partial w}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial w} \tag{II-C-21}$$

Dividing both sides of equation (II-C-20) by $\left(\frac{\partial z}{\partial u}\frac{\partial y}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial y}{\partial u}\right)$

we have

$$\frac{\partial x'}{\partial y} = \frac{\frac{\partial z}{\partial u}\frac{\partial x'}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial x'}{\partial u} + \frac{\partial z}{\partial v}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial u} - \frac{\partial z}{\partial u}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial v}}{\frac{\partial z}{\partial u}\frac{\partial y}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial y}{\partial u}} \tag{II-C-22}$$

and dividing both sides of equation (II-C-21) by $\left(\frac{\partial z}{\partial v}\frac{\partial y}{\partial w} - \frac{\partial z}{\partial w}\frac{\partial y}{\partial v}\right)$ we have

$$\frac{\partial x'}{\partial y} = \frac{\frac{\partial z}{\partial v}\frac{\partial x'}{\partial w} - \frac{\partial z}{\partial w}\frac{\partial x'}{\partial v} + \frac{\partial z}{\partial w}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial w}}{\frac{\partial z}{\partial v}\frac{\partial y}{\partial w} - \frac{\partial z}{\partial w}\frac{\partial y}{\partial v}} \tag{II-C-23}$$

Consequently the right side of equation (II-C-22) is equal to the right side of equation (II-C-23)

$$\frac{\frac{\partial z}{\partial u}\frac{\partial x'}{\partial v}-\frac{\partial z}{\partial v}\frac{\partial x'}{\partial u}+\frac{\partial z}{\partial v}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial u}-\frac{\partial z}{\partial u}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial v}}{\frac{\partial z}{\partial u}\frac{\partial y}{\partial v}-\frac{\partial z}{\partial v}\frac{\partial y}{\partial u}}$$

$$=\frac{\frac{\partial z}{\partial v}\frac{\partial x'}{\partial w}-\frac{\partial z}{\partial w}\frac{\partial x'}{\partial v}+\frac{\partial z}{\partial w}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial v}-\frac{\partial z}{\partial v}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial w}}{\frac{\partial z}{\partial v}\frac{\partial y}{\partial w}-\frac{\partial z}{\partial w}\frac{\partial y}{\partial v}}\,. \qquad \text{(II-C-24)}$$

Multiplying both sides of equation (II-C-24) by $\left(\frac{\partial z}{\partial v}\frac{\partial y}{\partial w}-\frac{\partial z}{\partial w}\frac{\partial y}{\partial v}\right)\left(\frac{\partial z}{\partial u}\frac{\partial y}{\partial v}-\frac{\partial z}{\partial v}\frac{\partial y}{\partial u}\right)$, we have

$$\left(\frac{\partial z}{\partial v}\frac{\partial y}{\partial w}-\frac{\partial z}{\partial w}\frac{\partial y}{\partial v}\right)\left(\frac{\partial z}{\partial u}\frac{\partial x'}{\partial v}-\frac{\partial z}{\partial v}\frac{\partial x'}{\partial u}+\frac{\partial x'}{\partial x}\frac{\partial z}{\partial v}\frac{\partial x}{\partial u}-\frac{\partial x'}{\partial x}\frac{\partial z}{\partial u}\frac{\partial x}{\partial v}\right)$$

$$=\left(\frac{\partial z}{\partial u}\frac{\partial y}{\partial v}-\frac{\partial z}{\partial v}\frac{\partial y}{\partial u}\right)\left(\frac{\partial z}{\partial v}\frac{\partial x'}{\partial w}-\frac{\partial z}{\partial w}\frac{\partial x'}{\partial v}+\frac{\partial x'}{\partial x}\frac{\partial z}{\partial w}\frac{\partial x}{\partial v}-\frac{\partial x'}{\partial x}\frac{\partial z}{\partial v}\frac{\partial x}{\partial w}\right).$$

(II-C-25)

Consequently it follows that

$$\frac{\partial x'}{\partial x}\left(\frac{\partial z}{\partial v}\frac{\partial x}{\partial u}-\frac{\partial z}{\partial u}\frac{\partial x}{\partial v}\right)\left(\frac{\partial z}{\partial v}\frac{\partial y}{\partial w}-\frac{\partial z}{\partial w}\frac{\partial y}{\partial v}\right)$$

$$+\left(\frac{\partial z}{\partial u}\frac{\partial x'}{\partial v}-\frac{\partial z}{\partial v}\frac{\partial x'}{\partial u}\right)\left(\frac{\partial z}{\partial v}\frac{\partial y}{\partial w}-\frac{\partial z}{\partial w}\frac{\partial y}{\partial v}\right) \qquad \text{(II-C-26)}$$

$$-\frac{\partial x'}{\partial x}\left(\frac{\partial z}{\partial w}\frac{\partial x}{\partial v}-\frac{\partial z}{\partial v}\frac{\partial x}{\partial w}\right)\left(\frac{\partial z}{\partial u}\frac{\partial y}{\partial v}-\frac{\partial z}{\partial v}\frac{\partial y}{\partial u}\right)$$

$$-\left(\frac{\partial z}{\partial v}\frac{\partial x'}{\partial w}-\frac{\partial z}{\partial w}\frac{\partial x'}{\partial v}\right)\left(\frac{\partial z}{\partial u}\frac{\partial y}{\partial v}-\frac{\partial z}{\partial v}\frac{\partial y}{\partial u}\right)$$

$$=0\,.$$

Equation (II-C-26) is then solved for $\frac{\partial x'}{\partial x}$ and we thus obtain

$$\frac{\partial x'}{\partial x} = \frac{\left[\left(\frac{\partial z}{\partial v}\frac{\partial x'}{\partial w} - \frac{\partial z}{\partial w}\frac{\partial x'}{\partial v}\right)\left(\frac{\partial z}{\partial u}\frac{\partial y}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial y}{\partial u}\right) - \left(\frac{\partial z}{\partial u}\frac{\partial x'}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial x'}{\partial u}\right)\left(\frac{\partial z}{\partial v}\frac{\partial y}{\partial w} - \frac{\partial z}{\partial w}\frac{\partial y}{\partial v}\right)\right]}{\left[\left(\frac{\partial z}{\partial v}\frac{\partial x}{\partial u} - \frac{\partial z}{\partial u}\frac{\partial x}{\partial v}\right)\left(\frac{\partial z}{\partial v}\frac{\partial y}{\partial w} - \frac{\partial z}{\partial w}\frac{\partial y}{\partial v}\right) - \left(\frac{\partial z}{\partial w}\frac{\partial x}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial x}{\partial w}\right)\left(\frac{\partial z}{\partial u}\frac{\partial y}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial y}{\partial u}\right)\right]} \quad \text{(II-C-27)}$$

Multiplying out the expressions in parentheses in equation (II-C-27) we have

$$\frac{\partial x'}{\partial x} = \frac{\left[\frac{\partial z}{\partial v}\frac{\partial x'}{\partial w}\frac{\partial z}{\partial u}\frac{\partial y}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial x'}{\partial w}\frac{\partial z}{\partial v}\frac{\partial y}{\partial u} - \frac{\partial z}{\partial w}\frac{\partial x'}{\partial v}\frac{\partial z}{\partial u}\frac{\partial y}{\partial v} + \frac{\partial z}{\partial w}\frac{\partial x'}{\partial v}\frac{\partial z}{\partial v}\frac{\partial y}{\partial u} - \frac{\partial z}{\partial u}\frac{\partial x'}{\partial v}\frac{\partial z}{\partial v}\frac{\partial y}{\partial w} + \frac{\partial z}{\partial u}\frac{\partial x'}{\partial v}\frac{\partial z}{\partial w}\frac{\partial y}{\partial v} + \frac{\partial z}{\partial v}\frac{\partial x'}{\partial u}\frac{\partial z}{\partial v}\frac{\partial y}{\partial w} - \frac{\partial z}{\partial v}\frac{\partial x'}{\partial u}\frac{\partial z}{\partial w}\frac{\partial y}{\partial v}\right]}{\left[\frac{\partial z}{\partial v}\frac{\partial x}{\partial u}\frac{\partial z}{\partial v}\frac{\partial y}{\partial w} - \frac{\partial z}{\partial v}\frac{\partial x}{\partial u}\frac{\partial z}{\partial w}\frac{\partial y}{\partial v} - \frac{\partial z}{\partial u}\frac{\partial x}{\partial v}\frac{\partial z}{\partial v}\frac{\partial y}{\partial w} + \frac{\partial z}{\partial u}\frac{\partial x}{\partial v}\frac{\partial z}{\partial w}\frac{\partial y}{\partial v} - \frac{\partial z}{\partial w}\frac{\partial x}{\partial v}\frac{\partial z}{\partial u}\frac{\partial y}{\partial v} + \frac{\partial z}{\partial w}\frac{\partial x}{\partial v}\frac{\partial z}{\partial v}\frac{\partial y}{\partial u} + \frac{\partial z}{\partial v}\frac{\partial x}{\partial w}\frac{\partial z}{\partial u}\frac{\partial y}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial x}{\partial w}\frac{\partial z}{\partial v}\frac{\partial y}{\partial u}\right]}, \quad \text{(II-C-28)}$$

Now the third term in the bracket constituting the numerator of the right side of equation (II-C-28) cancels the sixth term in this bracket. Likewise the fourth term in the bracket constituting the denominator of the right side of equation (II-C-28) cancels the fifth term in this bracket. The remaining terms in the numerator and denominator of the right side of equation (II-C-28) have a common factor $\frac{\partial z}{\partial p}$ which we next divide out. The terms that are then left are equivalent to the quotient of two Jacobian determinants. We thus have

$$\left(\frac{\partial x'}{\partial x}\right)_{y,z} = \frac{\begin{vmatrix} \frac{\partial x'}{\partial u} & \frac{\partial x'}{\partial v} & \frac{\partial x'}{\partial w} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \\ \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \end{vmatrix}}{\begin{vmatrix} \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} & \frac{\partial x}{\partial w} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \\ \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \end{vmatrix}}, \qquad \text{(II-C-29)}$$

provided the Jacobian determinant in the denominator is not equal to zero. Thus we obtain the result

$$\left(\frac{\partial x'}{\partial x}\right)_{y,z} = \frac{\dfrac{\partial(x', y, z)}{\partial(u, v, w)}}{\dfrac{\partial(x, y, z)}{\partial(u, v, w)}}. \qquad \text{(II-C-30)}$$

Similarly we have

$$\left(\frac{\partial x'}{\partial y}\right)_{x,z} = \frac{\dfrac{\partial(x', x, z)}{\partial(u, v, w)}}{\dfrac{\partial(y, x, z)}{\partial(u, v, w)}}. \qquad \text{(II-C-31)}$$

and

$$\left(\frac{\partial x'}{\partial z}\right)_{x,y} = \frac{\dfrac{\partial(x', x, y)}{\partial(u, v, w)}}{\dfrac{\partial(z, x, y)}{\partial(u, v, w)}} . \qquad \text{(II-C-32)}$$

Equations (II-C-30), (II-C-31), and (II-C-32) are not applicable, however, in the case of a one-component system of one phase and of variable mass when it is desired to transform the heat line integral from one coordinate space, such as the temperature-volume-mass coordinate space, to another coordinate space, such as the temperature-pressure-mass coordinate space, because the heat line integral depends upon the path and is not a function of the coordinates. In this case, to which the second equation of the heading of this Appendix applies, the transformation can be accomplished in the following way. Let us suppose that a line integral T

$$T = \int_{x_0, y_0, z_0}^{x, y, z} [P(x, y, z)dx + Q(x, y, z)dy + R(x, y, z)dz] \qquad \text{(II-C-33)}$$

depends upon the path, in which case, $\frac{\partial P}{\partial y} \neq \frac{\partial Q}{\partial x}$, $\frac{\partial P}{\partial z} \neq \frac{\partial R}{\partial x}$, and $\frac{\partial Q}{\partial z} \neq \frac{\partial R}{\partial y}$. This integral has no meaning unless further relations are given defining a particular path in (x, y, z)-space. For example, the curve can be represented in parametric form by the equations, $x = f(\alpha)$, $y = \phi(\alpha)$, and z = 5(o). We are next given that x» *y,* and *z* are functions of ii, v_9 and w_9

x = <£(u, v, *w)$_f$* *y* = x(ut v, *w),* *z* = ^(u, v, *w).* (II-C-34) (II-C-35) (II-C-36)

It is then desired to transform the integral *T* from (x, y* z)-space to (u_f K, uO-space. In this case if equations (II-C-34), (II-C-35), and (II-C-36) can be solved so that we have

a = *(x, *y, z),* *v* = X(x, y, z), u^ = *(x, y, z), (II-C-37) (II-C-38) (II-C-39)

then the curve in (x, y, z)-space can be transformed into the curve in (u, v, *w)-space* defined by the equations *u = F(s),* *v* = A(5), and v = 5(s). We next replace *dx* in the integral *T*

by ^ *du* / ou +^ *dv* / dv + ^ *dw* / dv/ $_9$ ^{f} also dy by ^ ^{J} |* du / du + |^ *dv* / du + |^ dv / 8^

and *dz by* $\frac{\partial z}{\text{on}}$ du + $\frac{\partial z}{\text{dv}}$ *dv* + $\frac{\partial z}{dw}$~ d^« We then have

$$\Gamma = \int^{u,\,v,\,w} \left\{ P\left[\frac{\partial x}{\partial u} \quad \cdot \frac{\partial x}{\partial v}\,dv + \frac{\partial x}{\partial w}\,dw\right] + Q\left[\frac{\partial y}{\partial u}\,du + \frac{\partial y}{\partial v}\,dv + \frac{\partial y}{\partial w}\,dw\right] + R\left[\frac{\partial z}{\partial u}\,du + \frac{\partial z}{\partial v}\,dv + \frac{\partial z}{\partial w}\,dw\right]\right\}, \qquad \text{(II-C-40)}$$

the curve in **(u_f v, v)-space** mow **being determined** by the equations $u = F(s)$, $v = A(s)$, $w = H(s)$. Consequently we thus obtain

$$T = \int_{u_0,\,v_0,\,w_0}^{u,\,v,\,w} \Big\{ P(\phi(u,v,w),\, \chi(u,v,w),\, \psi(u,v,w)) \left[\frac{\partial x}{\partial u}du + \frac{\partial x}{\partial v}dv + \frac{\partial x}{\partial w}dw\right]$$

$$+\, Q(\phi(u,v,w),\, \chi(u,v,w),\, \psi(u,v,w)) \left[\frac{\partial y}{\partial u}du + \frac{\partial y}{\partial v}dv + \frac{\partial y}{\partial w}dw\right]$$

$$+\, R(\phi(u,v,w),\, \chi(u,v,w),\, \psi(u,v,w)) \left[\frac{\partial z}{\partial u}du + \frac{\partial z}{\partial v}dv + \frac{\partial z}{\partial w}dw\right] \Big\}$$

$$= \int_{u_0,\,v_0,\,w_0}^{u,\,v,\,w} \{ \Theta(u,v,w)du + \Pi(u,v,w)dv + \Lambda(u,v,w)dw \}, \qquad \text{(II-C-41)}$$

where Θ is set equal to

$$P(\phi(u,v,w),\, \chi(u,v,w),\, \psi(u,v,w))\frac{\partial x}{\partial u}$$

$$+\, Q(\phi(u,v,w),\, \chi(u,v,w),\, \psi(u,v,w))\frac{\partial y}{\partial u}$$

$$+\, R(\phi(u,v,w),\, \chi(u,v,w),\, \psi(u,v,w))\frac{\partial z}{\partial u},$$

Π is set equal to

$$P(\phi(u,v,w),\, \chi(u,v,w),\, \psi(u,v,w))\frac{\partial x}{\partial v}$$

$$+\, Q(\phi(u,v,w),\, \chi(u,v,w),\, \psi(u,v,w))\frac{\partial y}{\partial v}$$

∂v .

and Q is set equal to

$$P(\phi(\text{u»}\ v,\ w)_9\ \text{x(u»}\ v_9\ \text{w}),\ \backslash p(u,\ v,\ \text{w}))\frac{dx}{dw}$$

$$+\,Q(\phi(\qquad\qquad\qquad\qquad))\frac{\partial y}{\partial w}$$

$$+\,R(\phi(u,\ v,\ w),\ x(u,\ v,\ w),\ \psi(u,\ v,\ w))\frac{\partial z}{\partial w}.$$

In order to evaluate?, Q, and /? as functions of u, v, and w we next solve the equations

$$\theta \quad - \quad \text{"\&} + Q\frac{\partial y}{\partial u} + R\frac{\partial z}{\partial u}, \qquad \text{(II-C-42)}$$

$$\Pi = P\frac{\partial x}{\partial v} + Q\frac{\partial y}{\partial v} + R\frac{\partial z}{\partial v}, \qquad \text{(II-C-43)}$$

and

$$\Omega = P\frac{\partial x}{\partial w} + Q\frac{\partial y}{\partial w} + R\frac{\partial z}{\partial w}, \qquad \text{(II-C-44)}$$

for P, θ, and i?. Thus we have

$$R\frac{\partial z}{\partial u} = \Theta - P\frac{\partial x}{\partial u} - Q\frac{\partial y}{\partial u}, \qquad \text{(II-C-45)}$$

$$\wedge \quad = \quad {}^{n}\ \text{"}\ {}^{p}\% \ - \ {}^{Q}\% \quad ' \qquad \text{(II-C-46)}$$

and

Dividing both sides of equation (II-C-45) by $\frac{\partial z}{\partial u}$, both sides of equation (II-C-46) by $\frac{\partial z}{\partial v}$, and both sides of equation (II-C-47) by $\frac{\partial z}{\partial w}$, we obtain

$$R = \Theta\Big/\frac{\partial z}{\partial u} - P\frac{\partial x}{\partial u}\Big/\frac{\partial z}{\partial u} - Q\frac{\partial y}{\partial u}\Big/\frac{\partial z}{\partial u} , \qquad \text{(II-C-48)}$$

$$R = \Pi\Big/\frac{\partial z}{\partial v} - P\frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v} - Q\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} , \qquad \text{(II-C-49)}$$

and

$$R = \Omega\Big/\frac{\partial z}{\partial w} - P\frac{\partial x}{\partial w}\Big/\frac{\partial z}{\partial w} - Q\frac{\partial y}{\partial w}\Big/\frac{\partial z}{\partial w} . \qquad \text{(II-C-50)}$$

Consequently we have

$$\Theta\Big/\frac{\partial z}{\partial u} - P\frac{\partial x}{\partial u}\Big/\frac{\partial z}{\partial u} - Q\frac{\partial y}{\partial u}\Big/\frac{\partial z}{\partial u} = \Pi\Big/\frac{\partial z}{\partial v} - P\frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v} - Q\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} , \qquad \text{(II-C-51)}$$

and

$$\Omega\Big/\frac{\partial z}{\partial w} - P\frac{\partial x}{\partial w}\Big/\frac{\partial z}{\partial w} - Q\frac{\partial y}{\partial w}\Big/\frac{\partial z}{\partial w} = \Pi\Big/\frac{\partial z}{\partial v} - P\frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v} - Q\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} . \qquad \text{(II-C-52)}$$

From equations (II-C-51) and (II-C-52) it follows that

$$Q\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - Q\frac{\partial y}{\partial u}\Big/\frac{\partial z}{\partial u} = \Pi\Big/\frac{\partial z}{\partial v} - \Theta\Big/\frac{\partial z}{\partial u} + P\frac{\partial x}{\partial u}\Big/\frac{\partial z}{\partial u} - P\frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v} \qquad \text{(II-C-53)}$$

and

$$Q\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - Q\frac{\partial y}{\partial w}\Big/\frac{\partial z}{\partial w} = \Pi\Big/\frac{\partial z}{\partial v} - \Omega\Big/\frac{\partial z}{\partial w} + P\frac{\partial x}{\partial w}\Big/\frac{\partial z}{\partial w} - P\frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v} . \qquad \text{(II-C-54)}$$

Dividing both sides of equation (II-C-53) by $\left(\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial u}\Big/\frac{\partial z}{\partial u}\right)$ and both sides of equation (II-C-54) by $\left(\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial w}\Big/\frac{\partial z}{\partial w}\right)$ we have

$$Q = \frac{\Pi\Big/\frac{\partial z}{\partial v} - \Theta\Big/\frac{\partial z}{\partial u} + P\left(\frac{\partial x}{\partial u}\Big/\frac{\partial z}{\partial u} - \frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v}\right)}{\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial u}\Big/\frac{\partial z}{\partial u}} \qquad \text{(II-C-55)}$$

and

$$Q = \frac{\Pi\Big/\frac{\partial z}{\partial v} - \Omega\Big/\frac{\partial z}{\partial w} + P\left(\frac{\partial x}{\partial w}\Big/\frac{\partial z}{\partial w} - \frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v}\right)}{\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial w}\Big/\frac{\partial z}{\partial w}} . \qquad \text{(II-C-56)}$$

Consequently we have

$$\frac{\Pi\Big/\frac{\partial z}{\partial v} - \Theta\Big/\frac{\partial z}{\partial u} + P\left(\frac{\partial x}{\partial u}\Big/\frac{\partial z}{\partial u} - \frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v}\right)}{\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial u}\Big/\frac{\partial z}{\partial u}}$$

$$= \frac{\Pi\Big/\frac{\partial z}{\partial v} - \Omega\Big/\frac{\partial z}{\partial w} + P\left(\frac{\partial x}{\partial w}\Big/\frac{\partial z}{\partial w} - \frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v}\right)}{\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial w}\Big/\frac{\partial z}{\partial w}} . \qquad \text{(II-C-57)}$$

Multiplying both sides of equation (II-C-57) by $\left(\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial u}\Big/\frac{\partial z}{\partial u}\right)\left(\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial w}\Big/\frac{\partial z}{\partial w}\right)$ we obtain

$$\left(\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial w}\Big/\frac{\partial z}{\partial w}\right)\left[\Pi\Big/\frac{\partial z}{\partial v} - \Theta\Big/\frac{\partial z}{\partial u} + P\left(\frac{\partial x}{\partial u}\Big/\frac{\partial z}{\partial u} - \frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v}\right)\right]$$

$$= \left(\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial u}\Big/\frac{\partial z}{\partial u}\right)\left[\Pi\Big/\frac{\partial z}{\partial v} - \Omega\Big/\frac{\partial z}{\partial w} + P\left(\frac{\partial x}{\partial w}\Big/\frac{\partial z}{\partial w} - \frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v}\right)\right] . \tag{II-C-58}$$

Solving equation (II-C-58) for P we have

$$P\left[\left(\frac{\partial x}{\partial u}\Big/\frac{\partial z}{\partial u} - \frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v}\right)\left(\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial w}\Big/\frac{\partial z}{\partial w}\right)\right.$$

$$\left. - \left(\frac{\partial x}{\partial w}\Big/\frac{\partial z}{\partial w} - \frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v}\right)\left(\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial u}\Big/\frac{\partial z}{\partial u}\right)\right]$$

$$= \left[\left(\Pi\Big/\frac{\partial z}{\partial v} - \Omega\Big/\frac{\partial z}{\partial w}\right)\left(\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial u}\Big/\frac{\partial z}{\partial u}\right)\right.$$

$$\left. - \left(\Pi\Big/\frac{\partial z}{\partial v} - \Theta\Big/\frac{\partial z}{\partial u}\right)\left(\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial w}\Big/\frac{\partial z}{\partial w}\right)\right] . \tag{II-C-59}$$

Carrying out the multiplications in equation (II-C-59) we obtain

$$
\begin{aligned}
P\Bigg[&\left(\frac{\partial x}{[illegible]} \Big/ [illegible]\right)[illegible]\ \frac{\partial z}{[illegible]} - \frac{\partial x}{[illegible]}\left([illegible]\right)\left(\frac{\partial y}{[illegible]} \Big/ \frac{\partial z}{[illegible]}\right) \\
&- \left(\frac{\partial x}{\partial v} \Big/ \frac{\partial z}{[illegible]}\right)\left([illegible]\right) \ [illegible]\ \frac{\partial x}{[illegible]}\left([illegible]\right)\left([illegible] \Big/ \frac{\partial z}{\partial w}\right) \\
&- \left(\frac{\partial x}{\partial w} \Big/ \frac{[illegible]}{\partial w}\right)\left(\frac{[illegible]}{\partial v} \Big/ \frac{[illegible]}{\partial v}\right) + \left(\frac{[illegible]}{\partial w} \Big/ \frac{[illegible]}{\partial w}\right)\left(\frac{[illegible]}{\partial u} \Big/ \frac{[illegible]}{\partial u}\right) \\
&+ \left(\frac{[illegible]}{\partial v} \Big/ \frac{[illegible]}{\partial v}\right)\left(\frac{[illegible]}{\partial v} \Big/ \frac{[illegible]}{\partial v}\right) [illegible] \left(\frac{[illegible]}{\partial v} \Big/ \frac{[illegible]}{\partial v}\right)\left(\frac{[illegible]}{\partial u} \Big/ \frac{[illegible]}{\partial u}\right)\Bigg] \\
= \Bigg[&\left(\Pi \Big/ \frac{\partial z}{\partial v}\right)\left(\frac{\partial y}{\partial v} \Big/ \frac{\partial z}{\partial v}\right) - \left(\Pi \Big/ \frac{\partial z}{\partial v}\right)\left(\frac{\partial y}{\partial u} \Big/ \frac{\partial z}{\partial u}\right) \\
&- \left(\Omega \Big/ \frac{\partial z}{\partial w}\right)\left(\frac{\partial y}{\partial v} \Big/ \frac{\partial z}{\partial v}\right) + \left(\Omega \Big/ \frac{\partial z}{\partial w}\right)\left(\frac{\partial y}{\partial u} \Big/ \frac{\partial z}{\partial u}\right)\Bigg] \\
+\Bigg[&\left(\Pi \Big/ \frac{\partial z}{\partial v}\right)\left(\frac{\partial y}{\partial w} \Big/ \frac{\partial z}{\partial w}\right) - \left(\Pi \Big/ \frac{\partial z}{\partial v}\right)\left(\frac{\partial y}{\partial v} \Big/ \frac{\partial z}{\partial v}\right) \\
&- \left(\Theta \Big/ \frac{\partial z}{\partial u}\right)\left(\frac{\partial y}{\partial w} \Big/ \frac{\partial z}{\partial w}\right) + \left(\Theta \Big/ \frac{\partial z}{\partial u}\right)\left(\frac{\partial y}{\partial v} \Big/ \frac{\partial z}{\partial v}\right)\Bigg] .
\end{aligned}
\tag{II-C-60}
$$

Equation (II-C-60) can then be rewritten as

$$P\left[\frac{\frac{dx}{du}\frac{dy}{dv}}{\frac{\partial z}{du}\frac{\partial z}{dv}} - \frac{\frac{dx}{du}\frac{\partial y}{dw}}{\frac{dz}{du}\frac{32}{dw}} - \frac{\frac{dx}{dv}\frac{dy}{dv}}{\frac{\partial z}{dv}\frac{\partial z}{dv}} + \frac{\frac{dx}{dv}\frac{iz}{\partial w}}{\frac{dz}{dv}\frac{32}{dw}}\right.$$

$$\left. - \frac{\frac{dx}{dw}\frac{dy}{dv}}{\frac{dz}{dw}\frac{dz}{dv}} + \frac{\frac{dx}{dw}\frac{hL}{du}}{\frac{dz}{dw}\frac{dz}{du}} \quad \frac{\frac{dx}{dv}\frac{dy}{dv}}{\frac{dz}{dv}\frac{dz}{dv}} - \frac{\frac{dx}{dv}\frac{\partial y}{du}}{\frac{dz}{dv}\frac{dz}{du}}\right]$$

$$= \left[\frac{11\,\frac{\partial y}{dv}}{\frac{dz}{dv}\frac{dz}{dv}} - \frac{n\,\frac{hL}{du}}{\frac{32}{dv}\frac{dz}{du}} - \frac{c\,\frac{\partial y}{dv}}{\frac{dz}{dw}\frac{dz}{dv}} + \frac{Q\,\frac{\partial y}{du}}{\frac{dz}{dw}\frac{dz}{du}}\right. \qquad \text{(II-C-61)}$$

$$\left. - \frac{n\,\frac{|z}{dv}}{\frac{\partial z}{dv}\frac{\partial z}{dv}} + \frac{n\,\frac{hL}{dw}}{\frac{32}{dv}\frac{\partial z}{\partial w}} + \frac{\Theta\,\frac{\partial y}{\partial v}}{Hii\;du\;dv} - \frac{\theta\,\frac{d£}{dw}}{\frac{dz}{du}\frac{dz}{dw}}\right] .$$

The third term in the bracket in the left side of equation **(II-C-61)** cancels the seventh term in this bracket and the first term in the bracket in the right side of equation **(II-C-61)** cancels the fifth term in this bracket. Multiplying the remaining terms in both sides of equation (II-C-61) by

$\left(\frac{\partial z}{\partial u}\, \frac{\partial z}{\partial v}\, \frac{\partial z}{\partial w}\right)$ we obtain

$$P\left[\frac{\partial x}{\partial u}\frac{\partial y}{\partial v}\frac{\partial z}{\partial w} - \frac{\partial x}{\partial u}\frac{\partial y}{\partial w}\frac{\partial z}{\partial v} + \frac{\partial x}{\partial v}\frac{\partial y}{\partial w}\frac{\partial z}{\partial u} - \frac{\partial x}{\partial w}\frac{\partial y}{\partial v}\frac{\partial z}{\partial u} + \frac{\partial x}{\partial w}\frac{\partial y}{\partial u}\frac{\partial z}{\partial v} - \frac{\partial x}{\partial v}\frac{\partial y}{\partial u}\frac{\partial z}{\partial w}\right]$$

$$= \Theta\left[\frac{\partial y}{\partial v}\frac{\partial z}{\partial w} - \frac{\partial y}{\partial w}\frac{\partial z}{\partial v}\right] + \Pi\left[\frac{\partial y}{\partial w}\frac{\partial z}{\partial u} - \frac{\partial y}{\partial u}\frac{\partial z}{\partial w}\right] + \Omega\left[\frac{\partial y}{\partial u}\frac{\partial z}{\partial v} - \frac{\partial y}{\partial v}\frac{\partial z}{\partial u}\right] \qquad \text{(II-C-62)}$$

Now $P(x, y, z)$ is the total derivative of Γ along a line parallel to the x-axis in (x, y, z)-space. Also $\Theta(u, v, w)$ is the total derivative of Γ along a line parallel to the u-axis in (u, v, w)-space, $\Pi(u, v, w)$ is the total derivative of Γ along a line parallel to the v-axis in (u, v, w)-space, and $\Omega(u, v, w)$ is the total derivative of Γ along a line parallel to the w-axis in (u, v, w)-space. Thus we have from equation (II-C-62)

$$P(x,y,z) = \left(\frac{\partial \Gamma}{\partial x}\right)_{y,z} = \frac{\begin{vmatrix} \frac{\partial \Gamma}{\partial u} & \frac{\partial \Gamma}{\partial v} & \frac{\partial \Gamma}{\partial w} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \\ \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \end{vmatrix}}{\begin{vmatrix} \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} & \frac{\partial x}{\partial w} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \\ \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \end{vmatrix}}. \qquad \text{(II-C-63)}$$

Likewise $Q(x, y, z)$ is the total derivative of T along a line parallel to the y-axis in (u, v, w)-space. Thus in a similar way we have

$$Q(x,y,z) = \left(\frac{\partial T}{\partial y}\right)_{x,z} = \frac{\begin{vmatrix} \frac{\partial T}{\partial u} & \frac{\partial T}{\partial v} & \frac{\partial T}{\partial w} \\ \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} & \frac{\partial x}{\partial w} \\ \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \end{vmatrix}}{\begin{vmatrix} \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \\ \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} & \frac{\partial x}{\partial w} \\ \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \end{vmatrix}} . \qquad \text{(II-C-64)}$$

Also $R(x, y, z)$ is the total derivative of T along a line parallel to the z-axis in (x, y, z)-space. Consequently in a similar way we have finally

$$R(x,y,z) = \left(\frac{\partial T}{\partial z}\right)_{x,y} = \frac{\begin{vmatrix} \frac{\partial T}{\partial u} & \frac{\partial T}{\partial v} & \frac{\partial T}{\partial w} \\ \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} & \frac{\partial x}{\partial w} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \end{vmatrix}}{\begin{vmatrix} \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \\ \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} & \frac{\partial x}{\partial w} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \end{vmatrix}} . \qquad \text{(II-C-65)}$$

Appendix D to Part II

Discussion of F.G. Donnanfs derivation of the equation *du = tds - pdv + \idm* for a one-component system of one phase and of variable mass

Donnan's[1] proof of the equation

du ≈ tds - pdv +]idm

for a one-component system of one phase and of variable mass is as follows:

> Applied to a homogeneous system characterized by a uniform temperature t and a uniform pressure p, and subject to no other external forces except that due to this pressure, the development of thermodynamics up to the date of Gibbsf researches may perhaps be briefly summarized in the equation of Clausius, 5u = t&s - *pSv,* where *u* = energy, *s* = entropy, and *v* = volume. This equation applies to a closed system of *constant* total mass, and the first fundamental step taken by Gibbs was to extend it to a system of *variable* mass. In the equation of Clausius the entropy of the system may be changed by the addition or subtraction of heat, whilst the volume may be altered by work done by or on the system, both types of change producing corresponding changes in the energy. It is possible, however, simultaneously to increase or diminish the energy, entropy, and volume of the system by increasing or diminishing its mass, whilst its internal physical state, as determined by its temperature and pressure, remains the same. If we are dealing with a system whose energy, entropy and

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[1] Donnan, F.G., *The Influence of* J. *Willard Gibbs on the Science of Physical Chemistry, An Address on the Occasion of the Centenary Celebration of the Founding of the Franklin Institute,* Philadelphia, The Franklin Institute, 1924, pp. 6, 7.

volume may be regarded as sensibly proportional, at constant temperature and pressure, to its mass, we may write:

$$du = 6u + u_0 dm$$

$$ds = 6s + s_0 dm$$

$$dv = Sv + v_o dm$$

where the total differentials du, ds_9 and *dv* indicate changes which take account of variation of mass at constant temperature and pressure as well as of heat and work effects at constant mass (indicated by the differentials 6u, 6s, *5v*) and u_o» *SQ,* v_{Qf} denote the energy, entropy, and volume, respectively, of unit mass under the specified conditions of temperature and pressure. Combining these equations with that of Clausius, we obtain

$$du = tds - pdv + (u_0 - ts_Q + pv_Q)dm$$

or, putting

$$u_0 - ts_0 + pvo = li$$

$$du = tds - pdv + udoi.$$

According to Donnan the total differentials du_f *ds,* and *dv* indicate the changes in *u* s,* and *v* which take account of variation of mass at constant temperature and constant pressure as well as of heat and **work** effects at constant mass. In **Donnan's** equation $du = 8u + uodm$ the term u^dm_9 *UQ* being the specific energy, gives the change in energy with mass at constant temperature and constant pressure; it does not give the change in energy with nass at constant entropy and constant volume. The independent variables in the right side of this equation are thus temperature, pressure, and mass. The differential δu is consequently really shorthand for $\frac{\partial u}{\partial t}dt + \frac{\partial u}{\partial p}dp$. Likewise in the equation $ds = \delta s + s_0 dm$, where s_0 is the specific entropy, the term δs is really shorthand for $\frac{\partial s}{\partial t}dt + \frac{\partial s}{\partial p}dp$. Similarly in the equation $dv = \delta v + v_0 dm$, where v_0 is the specific volume, the term δv is really shorthand for $\frac{\partial v}{\partial t}dt + \frac{\partial v}{\partial p}dp$. Thus written out in full we have

$$du = \frac{\partial u}{\partial t}dt + \frac{\partial u}{\partial p}dp + u_0 dm , \qquad \text{(II-D-1)}$$

$$ds = \frac{\partial s}{\partial t}dt + \frac{\partial s}{\partial p}dp + s_0 dm , \qquad \text{(II-D-2)}$$

and

$$dv = \frac{\partial v}{\partial t}dt + \frac{\partial v}{\partial p}dp + v_0 dm . \qquad \text{(II-D-3)}$$

Combining equations (II-D-1), (II-D-2) and (II-D-3) we have

$$du - t\,ds + p\,dv$$

$$= \frac{\partial u}{\partial t}dt + \frac{\partial u}{\partial p}dp - t\frac{\partial s}{\partial t}dt - t\frac{\partial s}{\partial p}dp + p\frac{\partial v}{\partial t}dt + p\frac{\partial v}{\partial p}dp$$

$$+ (u_0 - t s_0 + p v_0)dm . \qquad \text{(II-D-4)}$$

It is known from the case of a one-component system of one phase and constant mass that

$$\frac{\partial u}{\partial t} = m\left(\breve{c}_p - p\frac{\partial \breve{v}}{\partial t}\right), \qquad \text{(II-D-5)}$$

$$\frac{\partial u}{\partial p} = m\left(\breve{l}_p - p\frac{\partial \breve{v}}{\partial p}\right), \qquad \text{(II-D-6)}$$

$$\frac{\partial s}{\partial t} = m\frac{\breve{c}_p}{t}, \qquad \text{(II-D-7)}$$

$$\frac{\partial s}{\partial p} = m\frac{\breve{l}_p}{t}, \qquad \text{(II-D-8)}$$

$$\frac{\partial v}{\partial t} = m\frac{\partial \breve{v}}{\partial t}, \qquad \text{(II-D-9)}$$

and

$$\frac{\partial v}{\partial p} = m\frac{\partial \breve{v}}{\partial p}. \qquad \text{(II-D-10)}$$

Substituting these values of the partial derivatives of u and s from equations (II-D-5), (II-D-6), (II-D-7), (II-D-8), (II-P-9), and (II-D-10), in equation (II-D-4) we obtain

$$\begin{aligned} du - tds + pdv &= m\left(\breve{c}_p - p\frac{\partial \breve{v}}{\partial t}\right)dt + m\left(\breve{l}_p - p\frac{\partial \breve{v}}{\partial p}\right)dp - mt\frac{\breve{c}_p}{t}dt \\ &\quad - mt\frac{\breve{l}_p}{t}dp + mp\frac{\partial \breve{v}}{\partial t}dt + mp\frac{\partial \breve{v}}{\partial p}dp + (u_0 - ts_0 + pv_0)dm . \end{aligned} \qquad \text{(II-D-11)}$$

Thus we arrive at Donnan's equation

$$du = tds - pdv + (u_0 - ts_0 + pv_0)dm \,, \qquad \text{(II-D-12)}$$

but by this mode of derivation the independent variables are still t, p, and m, not s, v, and m.

The real problem Donnan was attempting to solve was to show that when the independent variables in the case of a one-component system of one phase and of variable mass are entropy, volume, and mass, the partial derivatives of the energy are $\frac{\partial u}{\partial s} = t$, $\frac{\partial u}{\partial v} = -p$, and $\frac{\partial u}{\partial m} = (u_0 - ts_0 + pv_0)$. In order to solve this problem Donnan had to begin with temperature, pressure, and mass as independent variables, because the change of energy with mass is only equal to the specific energy at constant temperature and constant pressure. The real problem then consists in a transformation from temperature, pressure, and mass as independent variables to entropy, volume, and mass as independent variables.

It is assumed that the equations

$$s = F(t,p,m) \qquad \text{(II-D-13)}$$

and

$$v = \phi(t,p,m) \qquad \text{(II-D-14)}$$

can be solved so that we have

$$t = F(s, v, m) \qquad \text{(II-D-15)}$$

and

$$p = \phi(s, v, m) \qquad \text{(II-D-16)}$$

and thus finally

$$u = \psi(s, v, m) \, . \qquad \text{(II-D-17)}$$

From equation (II-D-17) it follows that

$$du = \frac{\partial u}{\partial s} ds + \frac{\partial u}{\partial v} dv + \frac{\partial u}{\partial m} dm \, . \qquad \text{(II-D-18)}$$

The partial derivatives $\frac{\partial u}{\partial s}$, $\frac{\partial u}{\partial v}$, and $\frac{\partial u}{\partial m}$ are then obtainable by the use of the Jacobians in Tables (II-D-10), (II-D-12), and (II-D-14). Thus we have

$$\left(\frac{\partial u}{\partial s}\right)_{m,v} = \frac{\dfrac{\partial(u, m, v)}{\partial(t, p, m)}}{\dfrac{\partial(s, m, v)}{\partial(t, p, m)}} = \frac{-m^2\left\{t\left(\frac{\partial \breve{v}}{\partial t}\right)^2_{p,m} + \breve{c}_p\left(\frac{\partial \breve{v}}{\partial p}\right)_{t,m}\right\}}{-m^2\left\{\left(\frac{\partial \breve{v}}{\partial t}\right)^2_{p,m} + \frac{\breve{c}_p}{t}\left(\frac{\partial \breve{v}}{\partial p}\right)_{t,m}\right\}}$$

$$= t \, , \qquad \text{(II-D-19)}$$

$$\left(\frac{\partial u}{\partial v}\right)_{m,s} = \frac{\dfrac{\partial(u, m, s)}{\partial(t, p, m)}}{\dfrac{\partial(v, m, s)}{\partial(t, p, m)}} = \frac{-m^2\left\{p\left(\frac{\partial \breve{v}}{\partial t}\right)^2_{p,m} + \frac{p\breve{c}_p}{t}\left(\frac{\partial \breve{v}}{\partial p}\right)_{t,m}\right\}}{m^2\left\{\left(\frac{\partial \breve{v}}{\partial t}\right)^2_{p,m} + \frac{\breve{c}_p}{t}\left(\frac{\partial \breve{v}}{\partial p}\right)_{t,m}\right\}}$$

= [illegible] (II-D-20)

and

$$\left(\frac{\partial u}{\partial m}\right)_{v,s} = \frac{\dfrac{\partial(u, v, s)}{\partial(t, p, m)}}{\dfrac{\partial(m, v, s)}{\partial(t, p, m)}}$$

$$= \frac{-m^2\left\{\left[\frac{\breve{c}_p}{t}\left(\frac{\partial \breve{v}}{\partial p}\right)_{t,m} + \left(\frac{\partial \breve{v}}{\partial t}\right)^2_{p,m}\right](u_0 + pv_0 - ts_0)\right\}}{-m^2\left\{\frac{\breve{c}_p}{t}\left(\frac{\partial \breve{v}}{\partial p}\right)_{t,m} + \left(\frac{\partial \breve{v}}{\partial t}\right)^2_{p,m}\right\}}$$

$$= u_0 + pv_0 - ts_0 \,. \qquad \text{(II-D-21)}$$

In the case of a one-component system of one phase and of variable mass the chemical potential μ is equal to $\left(\frac{\partial u}{\partial m}\right)_{v,s}$ and consequently to $(u_0 + pv_0 - ts_0)$. Substituting the values of $\left(\frac{\partial u}{\partial s}\right)_{m,v}$, $\left(\frac{\partial u}{\partial v}\right)_{m,s}$, and $\left(\frac{\partial u}{\partial m}\right)_{v,s}$ from equations (II-D-19), (II-D-20), and (II-D-21) in equation (II-D-18) we arrive at the result

$$du = t\,ds - p\,dv + \mu\,dm \,, \qquad \text{(II-D-22)}$$

with s, v, and m as independent variables. Equation (II-D-22) is thus true with either t, p, and m as independent variables or with s, v, and m as independent variables. However, the more important significance of equation (II-D-22) is that it is true with s, v, and m as independent variables.

Part III

Relations between thermodynamic quantities and their first derivatives in a binary system of one phase and of unit mass

'Introduction

The basic thermodynamic relations for systems of variable composition were first derived by J. Willard Gibbs in his memoir entitled "On the Equilibrium of Heterogeneous Substances."[1] Gibbs[2] stated that the nature of the equations which express the relations between the energy, entropy, volume, and the quantities of the various components for homogeneous combinations of the substances in the given mass must be found by experiment. The manner in which the experimental determinations are to be carried out was indicated by him[3] in the following words: ffAs, however, it is only differences of energy and of entropy that can be measured, or indeed that have a physical meaning, the values of these quantities are so far arbitrary, that we may choose independently for each simple substance the state in which its energy and its entropy are both zero. The values of the

[1] Gibbs, J. Willard, Trans. Conn, Acad. of Arts and Sciences, 3, 108-248, 1874-78, or *Collected Works,* Longmans, Green and Company, New York, 1928, Vol. 1, pp. 55-184.

[2] Gibbs, J. Willard, Trans. Conn. Acad. of Arts and Sciences, 3, 140, 1874-78, or *Collected Works*, Longmans, Green and Company, New York, 1928, Vol. 1, p. 85.

[3] Gibbs, J. Willard, Trans. Conn. Acad. of Arts and Sciences, 3, 140-141, 1874-78, or *Collected Works,* Longmans, Green and Company, New York, 1928, Vol. 1, p. 85.

energy and the entropy of any compound body in any particular state will then be fixed. Its energy will be the sum of the work and heat expended in bringing its components from the states in which their energies and their entropies are zero into combination and to the state in question; and its entropy is the value of the integral $\int \frac{dQ}{t}$ for any reversible process by which that change is effected (dQ denoting an element of the heat communicated to the matter thus treated, and *t* the temperature of the matter receiving it)."

Calculation of the specific volume, the specific energy, and the specific entropy of a binary system of one phase as functions of the absolute thermodynamic temperature, the pressure, and the mass fraction of one component from experimental measurements[4]

In the case of a binary system of one phase, the mass fraction $\breve{m}_1$ of component 1 is defined by the equation

$$\breve{m}_1 \equiv \frac{m_1}{m_1 + m_2} , \qquad \text{(III-1)}$$

where m_1 denotes the mass of component 1 and m_2 denotes the

[4] Tunell, G., *Relations between Intensive Thernodynamic Quantities and Their First Derivatives in a Binary System of* 9nt> *Phase,* V.H. Freeman and Co., San Francisco and" London, *I9ti\ pr).* 7-16.

mass of component 2; the specific volume $\breve{V}$ is defined by the equation

$$\breve{V} \equiv \frac{V}{m_1 + m_2} \quad , \qquad \text{(III-2)}$$

where V denotes the total volume; the specific energy $\breve{U}$ *is* defined by the equation

$$\breve{U} = \frac{U}{mi + m_2} \quad , \qquad \text{(III-3)}$$

v/here £/ denotes the total energy; the specific entropy $\breve{S}$ is defined by the equation

$$\breve{S} \equiv \frac{S}{\cdot mi + m_2} \quad , \qquad \text{(III-4)}$$

v/here S denotes the total entropy. As a result of experiment it is known that the pressure p_9 the specific volume $\breve{V}_f$ the absolute thermodynamic temperature T, and the mass fraction *Si* of component 1 are connected by an equation of state

$$*(p_f \breve{V}* 7\backslash \breve{m}_1) = 0 \ , \qquad \text{(111-5)}$$

which can, in general, be solved for any one of these quantities as a function of the other three. The relation of the specific energy of such a system to the temperature, pressure, and sass fraction of component 1 is expressed by the equation

$$= \int_{T_0,\, p_0,\, \breve m_{1_0}}^{T,\, p,\, \breve m_1} \left\{ \left[\breve c_p - p\frac{\partial \breve V}{\partial T}\right] dT + \left[\breve l_p - p\frac{\partial \breve V}{\partial p}\right] dp + \frac{\partial \breve U}{\partial \breve m_1} d\breve m_1 \right\}, \qquad \text{(III-6)}$$

where $\breve c_p$ denotes the heat capacity at constant pressure per unit of mass and $\breve l_p$ denotes the latent heat of change of pressure at constant temperature per unit of mass. The relation of the specific entropy $\breve S$ to the temperature, pressure, and mass fraction of component 1 is expressed by the equation

$$\breve S(T, p, \breve m_1) - \breve S(T_0, p_0, \breve m_{1_0})$$

$$= \int_{T_0,\, p_0,\, \breve m_{1_0}}^{T,\, p,\, \breve m_1} \left\{ \frac{\breve c_p}{T} dT + \frac{\breve l_p}{T} dp + \frac{\partial \breve S}{\partial \breve m_1} d\breve m_1 \right\}. \qquad \text{(III-7)}$$

Necessary and sufficient conditions[5] for (III-6) are

$$\left\{ \frac{\partial \left[\breve l_p - p\frac{\partial \breve V}{\partial p}\right]}{\partial T} \right\}_{p,\, \breve m_1} = \left\{ \frac{\partial \left[\breve c_p - p\frac{\partial \breve V}{\partial T}\right]}{\partial p} \right\}_{T,\, \breve m_1}, \qquad \text{(III-S)}$$

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5 Osgood, W.F., *Advanced Calculus*, The Macmillan Company, New York, 1925, p. 232, and *Lehrbuch der Funktionentheorie*, Bd. 1, 5te Aufl., B.G. Teubner, Leipzig, 1928, pp. 142-150.

$$\left\{\frac{\partial \frac{\partial \breve{U}}{\partial \breve{m}_1}}{\partial T}\right\}_{p,\breve{m}_1} = \left\{\frac{\partial\left[\breve{c}_p - p\frac{\partial \breve{V}}{\partial T}\right]}{\partial \breve{m}_1}\right\}_{T,p}, \qquad \text{(III-9)}$$

and

$$\left\{\frac{\partial \frac{\partial \breve{U}}{\partial \breve{m}_1}}{\partial p}\right\}_{T,\breve{m}_1} = \left\{\frac{\partial\left[\breve{l}_p - p\frac{\partial \breve{V}}{\partial p}\right]}{\partial \breve{m}_1}\right\}_{T,p}. \qquad \text{(III-10)}$$

Similarly, necessary and sufficient conditions for (III-7) are

$$\left\{\frac{\partial \frac{\breve{l}_p}{T}}{\partial T}\right\}_{p,\breve{m}_1} = \left\{\frac{\partial \frac{\breve{c}_p}{T}}{\partial p}\right\}_{T,\breve{m}_1}, \qquad \text{(III-11)}$$

$$\left\{\frac{\partial \frac{\partial \breve{S}}{\partial \breve{m}_1}}{\partial T}\right\}_{p,\breve{m}_1} = \left\{\frac{\partial \frac{\breve{c}_p}{T}}{\partial \breve{m}_1}\right\}_{T,p}, \qquad \text{(III-12)}$$

and

$$\left\{\frac{\partial \frac{\partial \breve{S}}{\partial \breve{m}_1}}{\partial p}\right\}_{T,\breve{m}_1} = \left\{\frac{\partial \frac{\breve{l}_p}{T}}{\partial \breve{m}_1}\right\}_{T,p}. \qquad \text{(III-13)}$$

Carrying out the indicated differentiations in (III-8) and

(III–11) one obtains

$$\frac{\partial \breve{l}_p}{\partial T} - p\frac{\partial^2 \breve{V}}{\partial T \partial p} = \frac{\partial \breve{c}_p}{\partial p} - p\frac{\partial^2 \breve{V}}{\partial p \partial T} - \frac{\partial \breve{V}}{\partial T} \qquad \text{(III-14)}$$

and

$$\frac{1}{T}\frac{\partial \breve{l}_p}{\partial T} - \frac{\breve{l}_p}{T^2} = \frac{1}{T}\frac{\partial \breve{c}_p}{\partial p} . \qquad \text{(III-15)}$$

Combining (III-14) and (III-15) one has

$$\breve{l}_p = -T\frac{\partial \breve{V}}{\partial T} . \qquad \text{(III-16)}$$

Carrying out the indicated differentiations in (III-9) and (III-12) one obtains

$$\frac{\partial^2 \breve{U}}{\partial T \partial \breve{m}_1} = \frac{\partial \breve{c}_p}{\partial \breve{m}_1} - p\frac{\partial^2 \breve{V}}{\partial \breve{m}_1 \partial T} \qquad \text{(III-17)}$$

and

$$\frac{\partial^2 \breve{S}}{\partial T \partial \breve{m}_1} = \frac{1}{T}\frac{\partial \breve{c}_p}{\partial \breve{m}_1} . \qquad \text{(III-18)}$$

Combining (III-17) and (III-18) one has

$$\frac{\partial^2 \breve{U}}{\partial T \partial \breve{m}_1} = T\frac{\partial^2 \breve{S}}{\partial T \partial \breve{m}_1} - p\frac{\partial^2 \breve{V}}{\partial \breve{m}_1 \partial T} . \qquad \text{(III-19)}$$

Carrying out the indicated differentiations in (111-10) and (111-13) one obtains

$$\frac{\partial^2 \breve{U}}{\partial p \partial \breve{m}_1} = \frac{\partial \breve{l}_p}{\partial \breve{m}_1} - p\frac{\partial^2 \breve{V}}{\partial p \partial \breve{m}_1} \qquad \text{(III-20)}$$

and

$$\frac{\partial^2 \breve{S}}{\partial p \partial \breve{m}_1} = \frac{1}{T}\frac{\partial \breve{l}_p}{\partial \breve{m}_1} . \qquad \text{(111-21)}$$

Combining (111-20) and (111-21) one has

$$\frac{\partial^2 \breve{U}}{\partial p \partial \breve{m}_1} = T\frac{\partial^2 \breve{S}}{\partial p \partial \breve{m}_1} - p\frac{\partial^2 \breve{V}}{\partial \breve{m}_1 \partial p} . \qquad \text{(III-22)}$$

From (111-16) it follows that

$$\frac{\partial \breve{l}_p}{\partial T} = -T\frac{\partial^2 \breve{V}}{\partial T^2} - \frac{\partial \breve{V}}{\partial T} \qquad \text{(III-23)}$$

and from (111-14) and (111-16) one obtains

$$\frac{\partial \breve{C}_p}{\partial p} = -T\frac{\partial^2 \breve{V}}{\partial T^2} . \qquad \text{(III-24)}$$

From (111-16) it also follows that

$$\frac{\partial \breve{l}_p}{\partial p} = -T\frac{\partial^2 \breve{V}}{\partial p \partial T} \qquad \text{(III-25)}$$

and

$$\frac{\partial \breve{c}_p}{\partial \breve{m}_1} = -T\frac{\partial^2 \breve{V}}{\partial \breve{m}_1 \partial T} \ . \qquad \text{(III-26)}$$

Combining (III-26) and (III-20) one has

$$\frac{\partial^2 \breve{U}}{\partial T \partial \breve{m}_1} = -T\frac{\partial^2 \breve{V}}{\partial \breve{m}_1 \partial T} - p\frac{\partial^2 \breve{V}}{\partial \breve{m}_1 \partial p} \ , \qquad \text{(III-27)}$$

and, similarly, combining (III-26) and (III-21) one has

$$\frac{\partial^2 \breve{S}}{\partial p \partial \breve{m}_1} = -\frac{\partial^2 \breve{V}}{\partial \breve{m}_1 \partial T} \ . \qquad \text{(III-28)}$$

There is thus one relation, equation (III-16), between the seven quantities $\frac{\partial \breve{V}}{\partial T}$, $\frac{\partial \breve{V}}{\partial p}$, $\frac{\partial \breve{V}}{\partial \breve{m}_1}$, $\breve{c}_p$, $\frac{\partial \breve{\zeta}}{\partial \breve{m}_1}$, $\frac{\partial \breve{U}}{\partial \breve{m}_1}$, $\frac{\partial \breve{S}}{\partial \breve{m}_1}$. Consequently, all seven will be known if the following six are determined by means of experimental measurements: $\frac{\partial \breve{V}}{\partial T}$, $\frac{\partial \breve{V}}{\partial p}$, $\frac{\partial \breve{V}}{\partial \breve{m}_1}$, $\breve{c}_p$, $\frac{\partial \breve{U}}{\partial \breve{m}_1}$, $\frac{\partial \breve{S}}{\partial \breve{m}_1}$.

There are also eight relations, equations (III-17), (III-18), (III-23), (III-24), (III-25), (III-26), (III-27), (III-28), between the eighteen quantities, $\frac{\partial^2 \breve{V}}{\partial T^2}$, $\frac{\partial^2 \breve{V}}{\partial p^2}$, $\frac{\partial^2 \breve{V}}{\partial \breve{m}_1^2}$, $\frac{\partial^2 \breve{V}}{\partial T \partial p}$, $\frac{\partial^2 \breve{V}}{\partial T \partial \breve{m}_1}$, $\frac{\partial^2 \breve{V}}{\partial p \partial \breve{m}_1}$, $\frac{\partial c_p}{\partial T}$, $\frac{\partial c_p}{\partial p}$, $\frac{\partial c_p}{\partial m_1}$, $\frac{\partial \breve{c}_p}{\partial T}$, $\frac{\partial \breve{c}_p}{\partial p}$, $\frac{\partial \breve{c}_p}{\partial \breve{m}_1}$, $\frac{\partial^2 \breve{U}}{\partial T \partial \breve{m}_1}$, $\frac{\partial^2 \breve{U}}{\partial p \partial \breve{m}_1}$, $\frac{\partial^2 \breve{U}}{\partial \breve{m}_1^2}$, $\frac{\partial^2 \breve{S}}{\partial T \partial \breve{m}_1}$, $\frac{\partial^2 \breve{S}}{\partial p \partial \breve{m}_1}$, $\frac{\partial^2 \breve{S}}{\partial \breve{m}_1^2}$, by means of which from the following ten, $\frac{\partial \breve{V}}{\partial T}$, $\frac{\partial \breve{V}}{\partial p}$, $\frac{\partial \breve{V}}{\partial \breve{m}_1}$, $\frac{\partial^2 \breve{V}}{\partial T \partial p}$, $\frac{\partial^2 \breve{V}}{\partial T \partial \breve{m}_1}$, $\frac{\partial^2 \breve{V}}{\partial p \partial \breve{m}_1}$, $\frac{\partial \breve{C}_p}{\partial T}$, $\frac{\partial \breve{C}_p}{\partial \breve{m}_1}$, [illegible], [illegible], the remaining eight can be calculated. From equation (III-24) $\frac{\partial \breve{C}_p}{\partial p}$ can be calculated; from equation (III-23) $\frac{\partial \breve{l}_p}{\partial T}$ can be calculated; from equation (III-25) $\frac{\partial \breve{l}_p}{\partial p}$ can be calculated; from equation (III-26) $\frac{\partial \breve{l}_p}{\partial \breve{m}_1}$ can be calculated; from equation (III-17) $\frac{\partial^2 \breve{V}}{\partial T \partial \breve{m}_1}$ can be calculated; from equation (III-27) $\frac{\partial^2 \breve{V}}{\partial p \partial \breve{m}_1}$ can be calculated; from equation (III-18) $\frac{\partial^2 \breve{S}}{\partial T \partial \breve{m}_1}$ can be calculated; and from equation (III-28) $\frac{\partial^2 \breve{S}}{\partial p \partial \breve{m}_1}$ can be calculated. It will therefore suffice to determine experimentally $\frac{\partial \breve{V}}{\partial \breve{m}_1}$ along a line at constant temperature, T', and constant pressure, p', then to determine experimentally $\frac{\partial \breve{V}}{\partial T}$ at all points in a plane at constant pressure, p', and $\frac{\partial \breve{V}}{\partial p}$ at all points in $(T, p, \breve{m}_1)$-space, likewise to determine $\breve{C}_p$ at all points in a plane at constant pressure, p', and to determine experimentally $\frac{\partial \breve{l}_p}{\partial \breve{m}_1}$ along a line at constant temperature, T', and constant pressure, p', and also $\frac{\partial \breve{Z}}{\partial \breve{m}_1}$ along a line at constant temperature, T', and constant pressure, p'.

From measurements of specific volumes over the range of temperature, pressure, and composition that is of interest, the values of $\frac{\partial V}{\partial T}$, $\frac{\partial V}{\partial p}$ and $\frac{\partial V}{\partial m_1}$ can be obtained. By means of calorimetric measurements the necessary values of $\bar{C}_p$ can also be obtained. The determination of $\frac{\partial H}{\partial m_1}$ at constant temperature and pressure over the range of composition of interest can be accomplished in many cases by means of a constant volume calorimeter, and in some cases $\frac{\partial H}{\partial m_1}$ can be determined by means of measurements of the electromotive force of a galvanic ceil at constant pressure over the ranges of composition and temperature of interest in combination with the measurements of specific volume. The determination of $\frac{\partial \zeta}{\partial m_1}$ at constant temperature and pressure over the range of composition of interest can be accomplished most readily by measurements of the electromotive force of a galvanic cell at constant temperature and pressure if a suitable cell is available.

The methods of determination of $\frac{\partial \zeta}{\partial m_1}$ and $\frac{\partial H}{\partial m_1}$ by means of electromotive force Measurements can be illustrated by the following example. In the case of a galvanic cell consisting of electrodes which are liquid thallium amalgams of different concentrations both immersed in the same solution of a thallium salt, one has

$$\bar{G}_2 - \bar{G}_2' = -NF6 \quad ,^{6} \qquad (111\text{-}29)$$

where G denotes the Gibbs function, $U + pV - TS_9$ of a liquid thallium amalgam, $\bar{G}_2$ denotes the partial derivative (M.) V^no/m 7, p. ni at the concentration of one electrode, $\bar{G}_2'$ the same partial derivative at the concentration of the other electrode, n_2 the number of gram atoms of thallium, n_x the number of gram atoms of mercury, N the number of Faradays the passage of which through the cell accompanies the reversible transfer of one gram atom of thallium from the one amalgam to the other (N = 1 in this case since a pure thallous salt was used as the electrolyte), F the Faraday equivalent (which is equal to the charge of one electron times the number of atoms in a gram atom); and 6 the electromotive force. The values of the electromotive forces of a number of such cells, including one in which one electrode was a saturated liquid thallium amalgam, were determined at 20°C and 1 atmosphere by Richards and Daniels.[7] By measurement of the electromotive force of another galvanic cell in which the electrodes are finely divided pure crystalline thallium and thallium saturated liquid amalgam at the same temperature and pressure, the

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[6] Lewis, G. M.» and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances** McGraw-Hill Book Company, Inc., Mew York, 1923,. p. 265.

[7] Richards, T. W,, and F. .Daniels, Jour. Amer. Chen. Soc.f 41, 1732-1768, 1919.

difference $G_2^s - G_2$ could be evaluated, G_2^s denoting the value of $\bar{G}_2$ in the saturated liquid thallium amalgam, and G_2 the value of the function G for pure crystalline thallium per gram atom.[8] The value of G_2 being assumed known from measurements on pure thallium, the values of $\bar{G}_2$ in liquid amalgams of different concentrations are then obtainable from the measurements of electromotive force in the two kinds of cell. From the values of $\bar{G}_2$, the values of $\bar{G}_1 - G_1$ are calculable by the use of the equation

$$\bar{G}_1 - G_1 = -\int_0^{\hat{n}_2} \frac{\hat{n}_2}{\hat{n}_1} \frac{\partial \bar{G}_2}{\partial \hat{n}_2} \, d\hat{n}_2 \,, \tag{III-30}$$

[9]

where $\hat{n}_2$ denotes the gram atom fraction of thallium in the amalgams.

$$\hat{n}_2 \equiv \frac{n_2}{n_1 + n_2} \,, \tag{III-31}$$

and $\hat{n}_1$ the gram atom fraction of mercury,

$$\hat{n}_1 \equiv \frac{n_1}{n_1 + n_2} \,, \tag{III-32}$$

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[8] Richards, T.U., and F. Daniels, op. cit., pp. 1732-1768; Lewis, G.N., and M. Randall, op. cit., pp. 413-414.

[9] Lewis, G.N., and M. Randall, op. cit., p. 44; cf. also Gibbs, J. Willard, Trans. Conn. Acad. of Arts and Sciences, 3, 194, 1874-73, or *Collected Works,* Longmans, Green and Company, New York, 1925, Vol. 1, p. 135.

$\bar{G}_1$ the partial derivative $\left(\frac{\partial G}{\partial n_1}\right)_{T,\,p,\,n_2}$, and G_1^* the value of the function G for pure mercury per gram atom. The integrand in the integral on the right side of equation (III-30) remains finite and approaches a limit as n_2 approaches zero and the value of the integral is thus determinable.[10] The value of G_1^* is assumed to be known from

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[10] Gibbs showed that in the case of a solution in which the mass of the substance chosen as the solute is capable of negative values, the quantity $m_2\left(\frac{\partial \mu_2}{\partial m_2}\right)_{T,\,p,\,m_1}$ approaches zero as a limit when m_2 approaches zero, T, p, and m_1 being held constant, μ_2 denoting the derivative $\left(\frac{\partial \zeta}{\partial m_2}\right)_{T,\,p,\,m_1}$; he also showed that in the case of a solution in which the mass of the substance chosen as the solute is incapable of negative values, as is true of thallium amalgams, the quantity $m_2\left(\frac{\partial \mu_2}{\partial m_2}\right)_{T,\,p,\,m_1}$ still remains finite, and it approaches a limit greater than zero when m_2 approaches zero, T, p, and m_1 being held constant, even though the derivative $\left(\frac{\partial \mu_2}{\partial m_2}\right)_{T,\,p,\,m_1}$ becomes infinite in this case (Gibbs, J. Willard, Trans. Conn. Acad. of Arts and Sciences, 3, 194-196, 1874-78, or *Collected Works,* Longmans, Green and Company, New York, 1928, Vol. 1, pp. 135-137). It follows in the same way that the quantity $n_2\left(\frac{\partial \bar{G}_2}{\partial n_2}\right)_{T,\,p,\,n_1}$ also approaches a limit when n_2 approaches zero, T, p, and n_1 being held constant. By application of the change of variable theorem in partial

measurements on pure mercury, and hence $\bar{G}_1$ can be obtained as a function of the gram atom fraction at 20°C and 1 atmosphere. The derivative $\left(\frac{\partial G}{\partial m_2}\right)_{T,p,m_1}$ can be calculated from the equation

$$\left(\frac{\partial G}{\partial m_2}\right)_{T,p,m_1} = \frac{\bar{G}_2}{A_2}, \qquad \text{(III-33)}$$

where A_2 denotes the number of grams in a gram atom of thallium, and the derivative $\left(\frac{\partial G}{\partial m_1}\right)_{T,p,m_2}$ can be calculated

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differentiation one obtains the relation

$$\left(\frac{\partial \bar{G}_2}{\partial n_2}\right)_{T,p,n_1} = \left(\frac{\partial \bar{G}_2}{\partial \hat{n}_2}\right)_{T,p} \frac{n_1}{(n_1+n_2)^2}.$$

Multiplying both sides of this equation by n_2, one has

$$n_2\left(\frac{\partial \bar{G}_2}{\partial n_2}\right)_{T,p,n_1} = \left(\frac{\partial \bar{G}_2}{\partial \hat{n}_2}\right)_{T,p} \hat{n}_1\hat{n}_2.$$

Since $\hat{n}_1$ approaches 1 as a limit when n_2 approaches zero, T, p, and n_1 being held constant, it follows that $\hat{n}_2\left(\frac{\partial \bar{G}_2}{\partial \hat{n}_2}\right)_{T,p}$ approaches the same limit as $n_2\left(\frac{\partial \bar{G}_2}{\partial n_2}\right)_{T,p,n_1}$ and $n_2\left(\frac{\partial \bar{G}_2}{\partial n_2}\right)_{T,p,m_1}$.

from the equation

$$\left(\frac{\partial G}{\partial m_1}\right)_{T,\ p,\ m_2} = \frac{\overline{G}_1}{A_1}\ , \qquad \text{(III-34)}$$

where A_1 denotes the number of grams in a gram atom of mercury. The intensive function $\breve{G}$ is defined by the equation

$$G \quad E \quad \frac{G}{m_1 + m_2}\ . \qquad \text{(III-35)}$$

The derivative $\left(\frac{\partial \breve{G}}{\partial \breve{m}_1}\right)_{T,\ p}$ for liquid thallium amalgams at 20°C and 1 atmosphere can be calculated from the equation

$$\left(\frac{\partial \breve{G}}{\partial \breve{m}_1}\right)_{T,\ p} = \left(\frac{\partial G}{\partial m_1}\right)_{T,\ p,\ m_2} - \left(\frac{\partial G}{\partial m_2}\right)_{T,\ p,\ m_1}\ .^{11} \qquad \text{(III-36)}$$

By application of the Gibbs-Helmholtz equation

$$1_2 - \hat{H}_2 = NFT \,||\, - NF£ \ \wedge \qquad \text{(111-37)}$$

where H denotes the enthalpy, $U + pV_9$ of a liquid thallium amalgam, H_2 denotes the partial derivative $\left(\frac{\partial H}{\partial n_2}\right)_{T,\ p,\ n_1}$ and

[11] The derivation of equation (XII-36) is given in Appendix A to Part III.

[12] Lewis, G.N., and M. Randall, op. cit., pp. 172-173.

$\hat{H}_2$ the value of the function H for pure crystalline thallium per gram atom, the partial derivative $\bar{H}_2$ for liquid thallium amalgams could then be determined, provided the electromotive forces of the cells be measured over a range of temperature, the value of $\hat{H}_2$ being assumed known from measurements on pure crystalline thallium. From the values of $\bar{H}_2$, the values of $\bar{H}_1 - \hat{H}_1$ are calculable by the use of the equation

$$\bar{H}_1 - \hat{H}_1 = -\int_0^{\hat{n}_2} \frac{\hat{n}_2}{\hat{n}_1} \frac{\partial \bar{H}_2}{\partial \hat{n}_2}\, d\hat{n}_2 , \qquad \text{(III-38)}$$

where $\bar{H}_1$ denotes the partial derivative $\left(\frac{\partial H}{\partial n_1}\right)_{T,\,p,\,n_2}$ and $\hat{H}_1$ the value of the function H for pure mercury per gram atom. The value of $\hat{H}_1$ is assumed to be known from measurements on pure mercury, and hence $\bar{H}_1$ could be obtained as a function of the gram atom fraction at 20°C and 1 atmosphere. The derivative $\left(\frac{\partial H}{\partial m_2}\right)_{T,\,p,\,m_1}$ could be calculated from the equation

$$\left(\frac{\partial H}{\partial m_2}\right)_{T,\,p,\,m_1} = \frac{\bar{H}_2}{A_2} \qquad \text{(III-39)}$$

and the derivative $\left(\frac{\partial H}{\partial m_1}\right)_{T,\,p,\,m_2}$ could be calculated from the equation

(III-40)

The intensive function $\breve{H}$ is defined by the equation

$$\breve{H} \equiv \frac{H}{m_1 + m_2} \ . \qquad \text{(III-41)}$$

The derivative $\left(\frac{\partial \breve{H}}{\partial \breve{m}_1}\right)_{T,\,p}$ for liquid thallium amalgams at 20°C and 1 atmosphere could then be calculated from the equation

$$\left(\frac{\partial \breve{H}}{\partial \breve{m}_1}\right)_{T,\,p} = \left(\frac{\partial H}{\partial m_1}\right)_{T,\,p,\,m_2} - \left(\frac{\partial H}{\partial m_2}\right)_{T,\,p,\,m_1} \ [13] \qquad \text{(III-42)}$$

Alternatively, the function $\breve{H}$ of liquid thallium amalgams and the derivative $\left(\frac{\partial \breve{H}}{\partial \breve{m}_1}\right)_{T,\,p}$ could be calculated from calorimetric determinations of heats of mixing of thallium and mercury at constant pressure. Finally the values of $\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p}$ and $\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p}$ for liquid thallium **amalgams** at 20°C and 1 atmosphere could be calculated from the equations

$$\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} = \left(\frac{\partial \breve{H}}{\partial \breve{m}_1}\right)_{T,\,p} - p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p} \qquad \text{(III-43)}$$

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[13] **The derivation of equation (III-42) is given in Appendix A to Part III.**

and

$$\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p} = \frac{1}{T}\left[\left(\frac{\partial \breve{H}}{\partial \breve{m}_1}\right)_{T,\,p} - \left(\frac{\partial \breve{G}}{\partial \breve{m}_1}\right)_{T,\,p}\right]. \qquad \text{(III-44)}$$

Derivation of any desired relation between the intensive thermodynamic quantities, T, p, $\breve{m}_1$, $\breve{V}$, $\breve{U}$, $\breve{S}$, and their first derivatives for a binary system of one phase from the experimentally determined relations by the use of functional determinants (Jacobians)[14]

Equations (III-5), (III-6), and (III-7) can, in general, be solved for any three of the quantities, T, p, $\breve{m}_1$, $\breve{V}$, $\breve{U}$, $\breve{S}$, as functions of the remaining three. The first partial derivative of any one of the quantities, T, p, $\breve{m}_1$, $\breve{V}$, $\breve{U}$, $\breve{S}$, with respect to any second quantity when any third and fourth quantities are held constant can be obtained in terms of the six first derivatives, $\frac{\partial \breve{V}}{\partial T}$, $\frac{\partial \breve{V}}{\partial p}$, $\frac{\partial \breve{V}}{\partial \breve{m}_1}$, $\breve{C}_p$, $\frac{\partial \breve{U}}{\partial \breve{m}_1}$, $\frac{\partial \breve{S}}{\partial \breve{m}_1}$, together with the absolute thermodynamic temperature and the pressure, by application of the theorem[15] stating that, if $\psi = \omega(x, y, z)$, $x = f(u, v, w)$, $y = \varphi(u, v, w)$, $z = \chi(u, v, w)$,

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[14] Tunell, G., op. cit., pp. 17-23.

[15] A proof of this theorem for the case of functions of three independent variables is given in Appendix C to Part II.

then one has

$$\left(\frac{\partial x'}{\partial x}\right)_{y,z} = \frac{\begin{vmatrix} \frac{\partial x'}{\partial u} & \frac{\partial x'}{\partial v} & \frac{\partial x'}{\partial w} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \\ \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \end{vmatrix}}{\begin{vmatrix} \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} & \frac{\partial x}{\partial w} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \\ \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \end{vmatrix}} = \frac{\frac{\partial(x', y, z)}{\partial(u, v, w)}}{\frac{\partial(x, y, z)}{\partial(u, v, w)}}, \qquad \text{(III-45)}$$

provided all the partial derivatives in the determinants are continuous and provided the determinant in the denominator is not equal to zero.

In Tables III-1 to III-15 the value of the Jacobian is given for each set of three of the variables, T, p, m_1, V, U, S as x', y, z, or x, y, z, and with T, p, m_1 as u, v, w. There are sixty Jacobians in the Table, but one has

$$\frac{\partial(x, y, z)}{\partial(u, v, w)} = -\frac{\partial(z, y, x)}{\partial(u, v, w)} = \frac{\partial(y, z, x)}{\partial(u, v, w)}, \qquad \text{(III-46), (III-47)}$$

because interchanging two rows of a determinant changes the sign of the determinant. Hence it is only necessary to calculate the values of twenty of the sixty Jacobians. The calculations of these twenty Jacobians follow;

$$\frac{\partial(\breve{m}_1, T, p)}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial \breve{m}_1} \end{vmatrix}$$

$$= 1 \; ; \qquad \text{(111-48)}$$

$$\frac{\partial(\breve{V}, T, p)}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial \breve{m}_1} \end{vmatrix}$$

$$= \left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} \; ; \qquad \text{(111-49)}$$

$$\frac{\partial(\breve{U}, T, p)}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{U}}{\partial T} & \frac{\partial \breve{U}}{\partial p} & \frac{\partial \breve{U}}{\partial \breve{m}_1} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial \breve{m}_1} \end{vmatrix}$$

$$= \left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} \; ; \qquad \text{(111-50)}$$

$$\frac{\partial(\breve{S}, T, p)}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \dfrac{\partial \breve{S}}{\partial T} & \dfrac{\partial \breve{S}}{\partial p} & \dfrac{\partial \breve{S}}{\partial \breve{m}_1} \\ \dfrac{\partial T}{\partial T} & \dfrac{\partial T}{\partial p} & \dfrac{\partial T}{\partial \breve{m}_1} \\ \dfrac{\partial p}{\partial T} & \dfrac{\partial p}{\partial p} & \dfrac{\partial p}{\partial \breve{m}_1} \end{vmatrix}$$

$$= \left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p} ; \qquad \text{(III-51)}$$

$$\frac{\partial(\breve{V}, T, \breve{m}_1)}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \dfrac{\partial \breve{V}}{\partial T} & \dfrac{\partial \breve{V}}{\partial p} & \dfrac{\partial \breve{V}}{\partial \breve{m}_1} \\ \dfrac{\partial T}{\partial T} & \dfrac{\partial T}{\partial p} & \dfrac{\partial T}{\partial \breve{m}_1} \\ \dfrac{\partial \breve{m}_1}{\partial T} & \dfrac{\partial \breve{m}_1}{\partial p} & \dfrac{\partial \breve{m}_1}{\partial \breve{m}_1} \end{vmatrix}$$

$$= -\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1} ; \qquad \text{(III-52)}$$

$$\frac{\partial(\breve{U}, T, \breve{m}_1)}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \dfrac{\partial \breve{U}}{\partial T} & \dfrac{\partial \breve{U}}{\partial p} & \dfrac{\partial \breve{U}}{\partial \breve{m}_1} \\ \dfrac{\partial T}{\partial T} & \dfrac{\partial T}{\partial p} & \dfrac{\partial T}{\partial \breve{m}_1} \\ \dfrac{\partial \breve{m}_1}{\partial T} & \dfrac{\partial \breve{m}_1}{\partial p} & \dfrac{\partial \breve{m}_1}{\partial \breve{m}_1} \end{vmatrix}$$

$$= T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1} + p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1} ; \qquad \text{(III-53)}$$

$$\frac{\partial(\breve{S}, T, \breve{m}_1)}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} & \frac{\partial \breve{S}}{\partial \breve{m}_1} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \end{vmatrix}$$

$$= \left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}; \qquad (111\text{-}54)$$

$$\frac{\partial(\breve{U}, T, \breve{V})}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{U}}{\partial T} & \frac{\partial \breve{U}}{\partial p} & \frac{\partial \breve{U}}{\partial \breve{m}_1} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \end{vmatrix} \qquad (111\text{-}55)$$

$$= \left[\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1} + \left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1};$$

$$\frac{\partial(\breve{S}, T, \breve{V})}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} & \frac{\partial \breve{S}}{\partial \breve{m}_1} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \end{vmatrix}$$

$$= \left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1} + \left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}; \qquad (111\text{-}56)$$

$$\frac{\partial(\breve{S}, T, \breve{U})}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} & \frac{\partial \breve{S}}{\partial \breve{m}_1} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial \breve{U}}{\partial T} & \frac{\partial \breve{U}}{\partial p} & \frac{\partial \breve{U}}{\partial \breve{m}_1} \end{vmatrix}$$

$$= \left[\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1} - \left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p} \cdot p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1} ; \qquad \text{(III-57)}$$

$$\frac{\partial(\breve{V}, p, \breve{m}_1)}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial \breve{m}_1} \\ \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \end{vmatrix}$$

$$= \left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1} ; \qquad \text{(III-58)}$$

$$\frac{\partial(\breve{U}, p, \breve{m}_1)}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{U}}{\partial T} & \frac{\partial \breve{U}}{\partial p} & \frac{\partial \breve{U}}{\partial \breve{m}_1} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial \breve{m}_1} \\ \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \end{vmatrix}$$

$$= \breve{C}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1} ; \qquad \text{(III-59)}$$

$$\frac{\partial(\breve{S}, p, \breve{m}_1)}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} & \frac{\partial \breve{S}}{\partial \breve{m}_1} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial \breve{m}_1} \\ \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \end{vmatrix}$$

$$= \frac{\breve{C}_p}{T}, \qquad \text{(III-60)}$$

$$\frac{\partial(\breve{U}, p, \breve{V})}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{U}}{\partial T} & \frac{\partial \breve{U}}{\partial p} & \frac{\partial \breve{U}}{\partial \breve{m}_1} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial \breve{m}_1} \\ \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \end{vmatrix}$$

$$= -\left[\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} + \breve{C}_p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}; \qquad \text{(III-61)}$$

$$\frac{\partial(\breve{S}, p, \breve{V})}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} & \frac{\partial \breve{S}}{\partial \breve{m}_1} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial \breve{m}_1} \\ \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \end{vmatrix}$$

$$= \frac{\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} - \left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} \qquad \text{(III-62)}$$

$$\frac{\partial(\breve{S}, p, \breve{U})}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} & \frac{\partial \breve{S}}{\partial \breve{m}_1} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial \breve{m}_1} \\ \frac{\partial \breve{U}}{\partial T} & \frac{\partial \breve{U}}{\partial p} & \frac{\partial \breve{U}}{\partial \breve{m}_1} \end{vmatrix}$$

$$= \frac{\breve{c}_p}{T}\left[\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right] + \left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p} p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}; \tag{III-63}$$

$$\frac{\partial(\breve{U}, \breve{m}_1, \breve{V})}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{U}}{\partial T} & \frac{\partial \breve{U}}{\partial p} & \frac{\partial \breve{U}}{\partial \breve{m}_1} \\ \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \\ \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \end{vmatrix}$$

$$= -T\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} - \breve{c}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}; \tag{III-64}$$

$$\frac{\partial(\breve{S}, \breve{m}_1, \breve{V})}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} & \frac{\partial \breve{S}}{\partial \breve{m}_1} \\ \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \\ \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \end{vmatrix}$$

$$= -\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} - \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}; \tag{III-65}$$

$$\frac{\partial(\breve{S}, \breve{m}_1, \breve{U})}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} & \frac{\partial \breve{S}}{\partial \breve{m}_1} \\ \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \\ \frac{\partial \breve{U}}{\partial T} & \frac{\partial \breve{U}}{\partial p} & \frac{\partial \breve{U}}{\partial \breve{m}_1} \end{vmatrix}$$

$$= p\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\,\breve{m}_1} + \frac{p\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}; \qquad \text{(III-66)}$$

$$\frac{\partial(\breve{S}, \breve{V}, \breve{U})}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} & \frac{\partial \breve{S}}{\partial \breve{m}_1} \\ \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \\ \frac{\partial \breve{U}}{\partial T} & \frac{\partial \breve{U}}{\partial p} & \frac{\partial \breve{U}}{\partial \breve{m}_1} \end{vmatrix}$$

$$= \left[\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p}\right]\left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\,\breve{m}_1} + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right]. \qquad \text{(III-67)}$$

Table III-l
Jacobians of intensive functions
for a binary system of one phase

d(x', y, z) / 3(7\ p, m0 ' 3(x, v, z) / 3(T, p, ŏ0

x \ y, z	T, p
Si	1
V̆	(ĬS)
ŭ	(ft)
S	(ĭs)

Table III-2
Jacobians of intensive functions
for a binary system of one phase

$$\frac{\partial(x', y, z)}{\partial(T, p, \breve{m}_1)} \qquad \frac{\partial(x, y, z)}{\partial(T, p, m_1)}$$

x', x \ y, z	$T, \breve{m}_1$
p	-1
$\breve{V}$	$-\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$
$\breve{U}$	$T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} + p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$
$\breve{S}$	$\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}$

Table III-3 Jacobians of intensive functions for a binary system of one phase	
$\frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)}$ • [illegible]	
x \ y, z	$T, \breve{V}$
p	$-\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}$
$\breve{m}_1$	$\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$
$\breve{U}$	$\left[\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1} + \left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} \cdot T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}$
$\breve{S}$	$\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} + \left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$

Table III-4
Jacobians of intensive functions
for a binary system of one phase

$$\frac{\partial(x', y, z)}{\partial(T, p, \breve{m}_1)}, \quad \frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)}$$

x' / x \ y, z	$T, \breve{U}$
P	-(&),„
*,	$-T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} - p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$
$\breve{V}$	[-(S),p-KCiJ(4,-(t̆),p* T\d7)p, mi
$\breve{S}$	$\left[\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} - \left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p} \cdot p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$

Table III-5
Jacobians of intensive functions
for a binary system of one phase

$\frac{\partial(x', y, z)}{\partial(T, p, \breve{m}_1)}$, $\frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)}$

x \ y, z	r, s
p	[illegible]
[illegible]	$-\left(\frac{\partial \breve{V}}{\partial T}\right)$ pt ox
[illegible]	$-\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} - \left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$
$\breve{U}$	$\left[-\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} + \left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p} \cdot p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$

Table III-6
Jacobians of intensive functions
for a binary system of one phase

$$\frac{3(x', y, z)}{d(T, p, \breve{m}i)} \; f \; \frac{3(x, y, z)}{3(T, p_f r\breve{a}i)}$$

x' \ x	p,fI̊fx
T	1
V̆	*(dV̆)*
ŭ	c̆p-P\3̄r̄j – p. mi
s̆	**f̆a r**

Table III-7
Jacobians of intensive functions
for a binary system of one phase

$$\frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)}$$

\y, z / x'\	p, p
T	$\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}$
$\breve{m}_1$	p. mi
U	[- U*J T, p " p feJ T, J l a ? I Si + c pfej r, p
$\breve{S}$	rl»J T,p UxJ r,p U; p>Ji

Table III-8
Jacobians of intensive functions
for a binary system of one phase

\vf, z / x	p, Ŭ
	3(x', vt z) / 3(T, p, tfi) f **3(x, v, z)** / 3(T, p.tfi)
T	$\left(\frac{\partial \breve{U}}{\partial \breve{x}_1}\right)_{T,\ p}$
$\breve{x}_1$	- cP̆ + K3?j -
V	[/BŎX (%V̆ \ l/a?\ w/3?\ [U)n p* His,),.. Jvw),, ft - 'pfejr, p
S	l[(f,)7.p-Ki,),J*(f,)r.;Kii,,

Table III-9
Jacobians of intensive functions
for a binary system of one phase

$$\frac{\partial(x, y, z)}{\partial(T, p, \breve m_1)}, \quad \frac{\partial(x, y, z)}{\partial(T, p, \breve m_1)}$$

$x \backslash y, z$	$p, \breve S$
T	$\left(\frac{\partial \breve S}{\partial \breve m_1}\right)_{T,p}$
$\breve m_1$	$-\frac{\breve c_p}{T}$
$\breve V$	$-\frac{\breve c_p}{T}\left(\frac{\partial \breve V}{\partial \breve m_1}\right)_{T,p} + \left(\frac{\partial \breve S}{\partial \breve m_1}\right)_{T,p}\left(\frac{\partial \breve V}{\partial T}\right)_{p,\breve m_1}$
$\breve U$	$-\frac{\breve c_p}{T}\left[\left(\frac{\partial \breve U}{\partial \breve m_1}\right)_{T,p} - T\left(\frac{\partial \breve S}{\partial \breve m_1}\right)_{T,p}\right] - \left(\frac{\partial \breve S}{\partial \breve m_1}\right)_{T,p} \cdot p\left(\frac{\partial \breve V}{\partial T}\right)_{p,\breve m_1}$

Table III-10
Jacobians of intensive functions
for a binary system of one phase

$$\frac{\partial(x', y, z)}{\partial(T, p, \breve{m}_1)}, \quad \frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)}$$

x	$\breve{m}_1, \breve{V}$
T	$-\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$
P	$\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}$
U	JdV̆)^2 - ^\
$\breve{S}$	$-\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} - \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$

Table III-11
Jacobians of intensive functions
for a binary system of one phase

$$\frac{\partial(x', y, z)}{\partial(T, p, \breve{m}_1)} = \frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)}$$

y, z / x	$\breve{m}_1, \breve{V}$
T	$T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1} + p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}$
p	[illegible] $_{p,\breve{m}_1}$
$\breve{V}$	$T\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} + \breve{c}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}$
$\breve{S}$	$p\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} + \frac{p\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}$

Table III-12
Jacobians of intensive functions
for a binary system of one phase

$$\frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)} , \frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)}$$

y, z / x	$\breve{m}_1, \breve{S}$
T	$\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}$
P	$\breve{r}$
V	$\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} + \frac{\breve{C}_p}{T} \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$
S	[illegible]

Table III-13
Jacobians of intensive functions
for a binary system of one phase

$$\frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)} \qquad \frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)}$$

x \ y, z	$\breve{V}, \breve{U}$
T	$\left[\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1} + \left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T}$ [illegible]
p	$\left[-\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} - p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} + \breve{c}_p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}$
$\breve{m}_1$	$-T\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} - \breve{c}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$
$\breve{S}$	$\left[\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right]\left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right]$

Table III-14
Jacobians of intensive functions
for a binary system of one phase

$$\frac{\partial(x,y,z)}{\partial(T,p,\breve{m}_1)} , \frac{\partial(x,y,z)}{\partial(T,p,\breve{m}_1)}$$

x \ y, z	$\breve{V}, \breve{S}$
T	$\left(\frac{\partial\breve{V}}{\partial\breve{m}_1}\right)_{T,p}\left(\frac{\partial\breve{V}}{\partial T}\right)_{p,\breve{m}_1} + \left(\frac{\partial\breve{S}}{\partial\breve{m}_1}\right)_{T,p}\left(\frac{\partial\breve{V}}{\partial p}\right)_{T,\breve{m}_1}$
p	$\frac{\breve{C}_p}{T}\left(\frac{\partial\breve{V}}{\partial\breve{m}_1}\right)_{T,p} - \left(\frac{\partial\breve{S}}{\partial\breve{m}_1}\right)_{T,p}\left(\frac{\partial\breve{V}}{\partial T}\right)_{p,\breve{m}_1}$
$\breve{m}_1$	$-\left(\frac{\partial\breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} - \frac{\breve{C}_p}{T}\left(\frac{\partial\breve{V}}{\partial p}\right)_{T,\breve{m}_1}$
if	$\left[-\left(\frac{\partial\breve{U}}{\partial\breve{m}_1}\right)_{T,p} - p\left(\frac{\partial\breve{V}}{\partial\breve{m}_1}\right)_{T,p} + T\left(\frac{\partial\breve{S}}{\partial\breve{m}_1}\right)_{T,p}\right]\left[\left(\frac{\partial\breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} + \frac{\breve{C}_p}{T}\left(\frac{\partial\breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right]$

Table III-15
Jacobians of intensive functions
for a binary system of one phase

$$\frac{\partial(x', y, z)}{\partial(T, p, \breve{m}_1)}, \quad \frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)}$$

x \ y, z	$\breve{U}, \breve{S}$
T	[illegible] $\left(\frac{\partial \breve{K}}{\partial p}\right)$ [illegible]
p	$\frac{\breve{c}_p}{T}\left[\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p}$ [illegible] $T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]$ [illegible] $\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}$ [illegible] $p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}$
$\breve{m}_1$	$p\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} + \frac{p\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}$
$\breve{y}$	[illegible] $+ \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,}$ [illegible]

In order to obtain the first partial derivative of any one of the six quantities, T, p, $\breve{m}_1$, $\breve{V}$, $\breve{U}$, $\breve{S}$, with respect to any second quantity of the six when any third and fourth quantities of the six are held constant, one has only to divide the value of the Jacobian in which the first letter in the first line is the quantity being differentiated and in which the second and third letters in the first line are the quantities held constant by the value of the Jacobian in which the first letter of the first line is the quantity with respect to which the differentiation is taking place and in which the second and third letters in the first line are the quantities held constant.

To obtain the relation among any seven derivatives, having expressed them in terms of the same six derivatives,

$$\left(\frac{\partial \breve{V}}{\partial T}\right) \quad (\partial \breve{V} \quad (\partial \breve{V} \quad - \quad (\partial \breve{W} \quad \left(\partial \breve{S}\right)_{T,p},$$

one can then eliminate the six derivatives from the seven equations, leaving a single equation connecting the seven derivatives. In addition to the relations among seven derivatives there are also degenerate cases in which there are relations among fewer than seven derivatives.

An additional therraodynamic function $A \equiv U - TS$ is used to facilitate the solution of many problems. The corresponding intensive function $\breve{A}$ is defined by the equation

1 s S7T1£ • (m_68)

In case a relation is needed that involves one or more of the thermodynamic potential functions, $H,$ A_9 or $G*$ partial derivatives involving one or more of these functions can also be calculated as the quotients of two Jacobians, which can themselves be evaluated by the same method used to calculate the Jacobians in Tables III-l to 111-15.

Proof of the relation

$$\left(\frac{\partial \breve{G}}{\partial \breve{m}_1}\right)_{T,\,p} \qquad {}_{T,\,p,\,m_2} - \left(\frac{\partial G}{\partial m_2}\right)_{T,\,p,\,m_1}$$ [1]

The quantity $\breve{G}$ is defined by the equation

$$\breve{G} \equiv \frac{G}{} \quad . \qquad \text{(III-A-1)}$$

Multiplying both sides of equation (III-A-1) by (/??! + m_2) one has

$$G = \breve{G}\{m_x + m_2) \quad . \qquad \text{(III-A-2)}$$

Differentiating both sides of equation (III-A-2) with respect to *ai* holding T, p, and roa fast one obtains

$$\left(\quad {}^{l/}{}_{T,\,p\,\,fl?2} \qquad \right)_{T,\,p,\,m_2} \quad . \qquad \text{(III-A-3)}$$

The quantity *&* is a function of the temperature T» the pressure p* and the mass fraction $\breve{m}_x$. By application of the theorem for change of variables in partial differentiation one has thus

$$\left(\frac{\partial \breve{G}}{\partial m}\right)_{2\,«\,p?\,Jft2} = \left(\frac{\partial \breve{G}}{\partial \breve{m}}\right)_{J-\,f\,p} \left(\frac{\partial \breve{m}_1}{\partial \hat{m}_1}\right)_{1\,*\,pt\,UI2} , \qquad \text{(III-A-4)}$$

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[1] Tunell, G., Amer, Jour. Sci., 255, 261-265, 1957, and Tunell, G,, *Relations between Intensive Thermodynamic Quantities and Their First Derivatives in a Binary System of One Phaset* W.H. Freeman and Co., San Francisco and London, 1960, pp. 25, 26.

Since, by definition,

$$\breve{m}_1 \equiv \frac{m_1}{m_1 + m_2} , \qquad \text{(III-A-5)}$$

one has

$$\left(\frac{\partial \breve{m}_1}{\partial m_1}\right)_{T,\,p,\,m_2} = \frac{1}{m_1 + m_2} - \frac{m_1}{(m_1 + m_2)^2}$$

$$= \frac{m_2}{(m_1 + m_2)^2} . \qquad \text{(III-A-6)}$$

Hence it follows that

$$\left(\frac{\partial G}{\partial m_1}\right)_{T,\,p,\,m_2} = \breve{G} + (m_1 + m_2)\left(\frac{\partial \breve{G}}{\partial \breve{m}_1}\right)_{T,\,p} \frac{m_2}{(m_1 + m_2)^2}$$

$$= \breve{G} + \breve{m}_2\left(\frac{\partial \breve{G}}{\partial \breve{m}_1}\right)_{T,\,p} , \qquad \text{(III-A-7)}$$

and, similarly,

$$\left(\frac{\partial G}{\partial m_2}\right)_{T,\,p,\,m_1} = \breve{G} + \breve{m}_1\left(\frac{\partial \breve{G}}{\partial \breve{m}_2}\right)_{T,\,p}$$

$$= \breve{G} - \breve{m}_1\left(\frac{\partial \breve{G}}{\partial \breve{m}_1}\right)_{T,\,p} . \qquad \text{(III-A-8)}$$

By subtracting the left side of equation (III-A-8) from the left side of equation (III-A-7) and the right side of equation (III-A-8) from the right side of equation (III-A-7), one thus obtains the equation to be proved:

$$\left(\frac{\partial \breve{G}}{\partial \breve{m}_1}\right)_{T,\,p} = \left(\frac{\partial G}{\partial m_1}\right)_{T,\,p,\,m_2} - \left(\frac{\partial G}{\partial m_2}\right)_{T,\,p,\,m_1} . \qquad \text{(III-A-9)}$$

In a similar way the equation

$$\left(\frac{\partial \breve{H}}{\partial \breve{m}_1}\right)_{T,\,p} = \left(\frac{\partial H}{\partial m_1}\right)_{T,\,p,\,m_2} - \left(\frac{\partial H}{\partial m_2}\right)_{T,\,p,\,m_1} \qquad \text{(III-A-10)}$$

can also be derived.

Appendix B to Part III

Transformation of the work and heat line integrals from one coordinate space to other coordinate spaces in the case of a binary system of one phase and of unit mass

As in the case of a one component system of one phase and of variable mass, it is also true in the case of a binary system of one phase and of unit mass that it is not necessary to define either work or heat when masses are being transferred to or from the system to change its composition in order to obtain the energy and the entropy as functions of the absolute thermodynamic temperature, the pressure, and the mass fraction of one component from experimental measurements. Thus the derivation of the Jacobians listed in Tables III-l to III—15 did not depend upon definitions of work or heat in the case of a binary system of one phase and of unit mass when masses are being transferred to or from the system to change its composition.

For some purposes, however, it is useful to have definitions of work done and heat received in the case of a binary system of one phase and of unit mass when masses are being transferred to or from the system to change its composition. If the conclusion of Van Wylen and Professor Uild be accepted that it cannot be said that work is done at a stationary boundary across which mass is transported, then the work *I'!* done by a binary system of one phase and of unit mass can be represented by the line integral

$$\int_{T_0,\, p_0,\, \breve{m}_{1_0}}^{T,\, p,\, \breve{m}_1} \left\{ p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1} dT + p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1} dp + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\, p} d\breve{m}_1 \right\} \quad \text{(III-B-1)}$$

in $(T, p, \breve{m}_1)$-space. Furthermore, in the case of such a system the heat Q received can be represented by the line integral

$$Q = \int_{T_0,\, p_0,\, \breve{m}_{1_0}}^{T,\, p,\, \breve{m}_1} \left\{ \left(\frac{dQ}{dT}\right)_{p,\, \breve{m}_1} dT + \left(\frac{dQ}{dp}\right)_{T,\, \breve{m}_1} dp + \left(\frac{dQ}{d\breve{m}_1}\right)_{T,\, p} d\breve{m}_1 \right\}$$

$$= \int_{\ldots\, \breve{m}_{1_0}}^{T,\, p,\, \breve{m}_1} \Big\{ [\text{illegible}] \Big(\ldots\Big)_{T,\, p} d\breve{m}_1 \Big\} . \quad \text{(III-B-2)}$$

In order to obtain the total derivative of the work done along a straight line parallel to one of the coordinate axes in any other coordinate space one obtains from Tables III-1 to III-15 the partial derivative of the volume with respect to the quantity plotted along, that axis when the quantities plotted along the other axes are held constant and one multiplies this partial derivative by the pressure. The total derivative of the heat received along a straight line parallel to one of the coordinate axes in any other space, on the other hand, cannot be obtained by multiplication of the partial derivative of the entropy by the absolute thermodynamic temperature when transfer of masses to or from the system is involved. In such cases the total derivatives of the heat received along lines parallel to the coordinate axes in any desired coordinate space can be derived in terms of the total derivatives of the heat received along lines parallel to the coordinate axes in $(T, p, \breve{m}_1)$-space by transformation of the heat line integrals by the use of the method set forth in the second half of Appendix B to Part II. Following is an example of such a transformation. In the case of a binary system of one phase and of unit mass the heat line integral extended along a path in $(T, \breve{m}_1, \breve{V})$-space is

$$Q = \int_{T_0,\, \breve{m}_{1_0},\, \breve{V}_0}^{T,\, \breve{m}_1,\, \breve{V}} \left\{ \left(\frac{dQ}{dT}\right)_{\breve{m}_1,\, \breve{V}} dT + \left(\frac{dQ}{d\breve{m}_1}\right)_{T,\, \breve{V}} d\breve{m}_1 + \left(\frac{dQ}{d\breve{V}}\right)_{T,\, \breve{m}_1} d\breve{V} \right\}$$

$$= \int_{T_0,\, \breve{m}_{1_0},\, \breve{V}_0}^{T,\, \breve{m}_1,\, \breve{V}} \left\{ \breve{c}_V dT + \left(\frac{dQ}{d\breve{m}_1}\right)_{T,\, \breve{V}} d\breve{m}_1 + l_V d\breve{V} \right\} . \qquad \text{(III-B-3)}$$

The derivatives $\left(\frac{\partial Q}{\partial T}\right)_{\breve m_1,\breve V}$, $\left(\frac{\partial Q}{\partial \breve m_1}\right)_{T,\breve V}$, and $\left(\frac{\partial Q}{\partial \breve V}\right)_{T,\breve m_1}$ can be evaluated by the method set forth in the second half of Appendix B to part II as the quotients of two determinants. Thus we have

$$\left(\frac{\partial Q}{\partial T}\right)_{\breve m_1,\breve V} = \breve c_v = \frac{\begin{vmatrix} \frac{\partial Q}{\partial T} & \frac{\partial Q}{\partial p} & \frac{\partial Q}{\partial \breve m_1} \\ \frac{\partial \breve m_1}{\partial T} & \frac{\partial \breve m_1}{\partial p} & \frac{\partial \breve m_1}{\partial \breve m_1} \\ \frac{\partial \breve V}{\partial T} & \frac{\partial \breve V}{\partial p} & \frac{\partial \breve V}{\partial \breve m_1} \end{vmatrix}}{\begin{vmatrix} \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve m_1} \\ \frac{\partial \breve m_1}{\partial T} & \frac{\partial \breve m_1}{\partial p} & \frac{\partial \breve m_1}{\partial \breve m_1} \\ \frac{\partial \breve V}{\partial T} & \frac{\partial \breve V}{\partial p} & \frac{\partial \breve V}{\partial \breve m_1} \end{vmatrix}}$$

$$= \left[\left(\frac{\partial Q}{\partial p}\right)_{T,\breve m_1}\left(\frac{\partial \breve V}{\partial T}\right)_{p,\breve m_1} - \left(\frac{\partial Q}{\partial T}\right)_{p,\breve m_1}\left(\frac{\partial \breve V}{\partial p}\right)_{T,\breve m_1}\right] \div \left[-\left(\frac{\partial \breve V}{\partial p}\right)_{T,\breve m_1}\right]$$

$$= \left[\breve c_p\left(\frac{\partial \breve V}{\partial p}\right)_{T,\breve m_1} - \breve l_p\left(\frac{\partial \breve V}{\partial T}\right)_{p,\breve m_1}\right] \div \left(\frac{\partial \breve V}{\partial p}\right)_{T,\breve m_1}$$

$$= \left[\breve c_p\left(\frac{\partial \breve V}{\partial p}\right)_{T,\breve m_1} + T\left(\frac{\partial \breve V}{\partial T}\right)^2_{p,\breve m_1}\right] \div \left(\frac{\partial \breve V}{\partial p}\right)_{T,\breve m_1}, \qquad \text{(III-B-4)}$$

and

$$\left(\frac{\partial Q}{\partial \breve{m}_1}\right)_{T,\breve{V}} = \frac{\begin{vmatrix} \frac{\partial Q}{\partial T} & \frac{\partial Q}{\partial p} & \frac{\partial Q}{\partial \breve{m}_1} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \end{vmatrix}}{\begin{vmatrix} \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \end{vmatrix}}$$

$$= \left[\left(\frac{\partial Q}{\partial \breve{m}_1}\right)_{T,p}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1} - \left(\frac{\partial Q}{\partial p}\right)_{T,\breve{m}_1}\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right] \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}$$

$$= \left[\left(\frac{\partial Q}{\partial \breve{m}_1}\right)_{T,p}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1} - \Lambda_p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right] \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}$$

$$= \left[\left(\frac{\partial Q}{\partial \breve{m}_1}\right)_{T,p}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1} + T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right] \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}$$

(1II-B-5)

and finally

$$\left(\frac{đQ}{\partial \breve{V}}\right)_{T,\,\breve{m}_1} = \breve{l}_V = \frac{\begin{vmatrix} \frac{đQ}{\partial T} & \frac{đQ}{\partial p} & \frac{đQ}{\partial \breve{m}_1} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \end{vmatrix}}{\begin{vmatrix} \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \end{vmatrix}}$$

$$= \left[-\left(\frac{đQ}{\partial p}\right)_{T,\,\breve{m}_1}(1)\right] \div \left[-\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right]$$

$$= \left[\breve{l}_p\right] \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}$$

$$= \left[-T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}\right] \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1} . \qquad \text{(III-B-6)}$$

Part IV

Relations betv/een thermodynamic quantities and their first derivatives in a binary system of one phase and of variable total mass

Introduction

In the following text the relations for the energy and the entropy of a binary system of one phase and of variable total mass are derived and a table of Jacobians is presented by means of which any first partial derivative of any one of the quantities, absolute thermodynamic temperature T_9 pressure p, mass *mi* of component 1, mass m_2 of component 2, total volume V_f total energy U_9 and total entropy *S,* with respect to any other of these quantities can be obtained in terms of the partial derivative of the specific volume *V* with respect to the absolute thermodynamic temperature, the partial derivative of the specific volume with respect to the pressure, the partial derivative of the specific volume with respect to the mass fraction *Si* of component 1, the heat capacity at constant pressure per unit of mass $\breve{C}p$, the partial derivative of the specific energy $\breve{U}$ with respect to the mass fraction of component 1, the partial derivative of the specific entropy $\breve{S}$ with respect to the mass fraction of component 1, and certain of the quantities, 7\ *p,* mi, m_{29}f$\breve{T}$li»S_2* $\breve{V}$, $\breve{U}$, $\breve{S}$, where $\breve{m}_2$ denotes the mass fraction of component 2.

Calculation of the total volume, the total energy, and the total entropy of a binary system of one phase and of variable total mass as functions of the absolute thermodynamic temperature, the pressure, and the masses of components *one* and two

Thermodynamic formulas can be developed in the case of a binary system of one phase and of variable total mass on the basis of the following set of variable quantities: the absolute thermodynamic temperature, the pressure, the mass of component 1, the mass of component 2, the total volume, the total energy, the total entropy, the mass fraction of component 1, the mass fraction of component 2, the specific volume, the specific energy, the specific entropy, the heat capacity at constant pressure per unit of mass, and the latent heat of change of pressure at constant temperature per unit of mass (p.

In the case of a binary system of one phase and of variable total mass the total volume is a function of the absolute thermodynamic temperature, the pressure, the mass of component 1, and the mass of component 2,

$$V = f(T, p, m_1, m_2) . \qquad \text{(IV-1)}$$

The total volume is equal to the total mass times the specific volume

$$V = (m_1 + m_2)\breve{V} , \qquad \text{(IV-2)}$$

and the specific volume is a function of the absolute thermodynamic temperature, the pressure, and the mass fraction of component 1,

$$\breve{V} = \breve{V}(T, p, \breve{m}_1) . \qquad \text{(IV-3)}$$

From equations (IV-1), (IV-2), and (IV-3) it then follows that

$$\left(\frac{\partial V}{\partial T}\right)_{p, m_1, m_2} = (m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} , \qquad \text{(IV-4)}$$

$$\left(\frac{\partial V}{\partial p}\right)_{T, m_1, m_2} = (m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1} , \qquad \text{(IV-5)}$$

$$\left(\frac{\partial V}{\partial m_1}\right)_{T, p, m_2} = \breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} , \qquad \text{(IV-6)}$$

and

$$\left(\frac{\partial V}{\partial m_2}\right)_{T, p, m_1} = \breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} . \qquad \text{(IV-7)}$$

The total energy is a function of the absolute thermodynamic temperature, the pressure, the mass of component 1, and the mass of component 2

$$U = U(T, p, m_1, m_2) . \qquad \text{(IV-8)}$$

As in the case of a one–component system of one phase and of variable mass it is known from experiment that the energy is an extensive function* Thus the total energy is equal to the total mass times the specific energy

$$U = \text{Oi} + m_2)\breve{U} \ . \qquad \text{(IV-9)}$$

Furthermore it is known that the specific energy is a function of the absolute thermodynaraic temperature, the pressure, and the mass fraction of component 1,

$$\breve{U} = \theta(T, p, \breve{m}i) \bullet \qquad \text{(IV-10)}$$

Thus the relation of the total energy to the absolute thermodynamic temperature, the pressure, the mass of component 1, and the mass of component 2 is expressed by the equation

C/(T, *p$* fl?j» ^2) ~ *U(TQ§* po» ^i_n> ^ro2_ft)

$$= \int_{T<>f \ pot \ m_{1_0}, m_{2_0}}^{Tf \ p, \ mi_9 \ m_2} \left[(/D! + DJ_2) j?p - P \frac{\partial \breve{V}}{} fl \right] dT + (mx + m_2) \left[7_p - P \wedge \right] dp$$

$$+ \frac{\partial U}{\partial m_1} dm_1 + \frac{\partial U}{\partial m_2} dm_2 \Big\} \ . \qquad \text{(IV-11)}$$

From equations (IV-8), (IV-9), (IV-10), and (IV-11) it

follows that

$$\left(\frac{\partial U}{\partial T}\right)_{p,\,m_1,\,m_2} = (m_1 + m_2)\left[\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}\right], \qquad \text{(IV-12)}$$

$$\left(\frac{\partial U}{\partial p}\right)_{T,\,m_1,\,m_2} = (m_1 + m_2)\left[\breve{l}_p - p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right], \qquad \text{(IV-13)}$$

$$\left(\frac{\partial U}{\partial m_1}\right)_{T,\,p,\,m_2} = \breve{U} + \breve{m}_2\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p}, \qquad \text{(IV-14)}$$

and

$$\left(\frac{\partial U}{\partial m_2}\right)_{T,\,p,\,m_1} = \breve{U} - \breve{m}_1\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p}. \qquad \text{(IV-15)}$$

The total entropy is a function of the absolute thermodynamic temperature, the pressure, the mass of component 1, and the mass of component 2

$$S = S(T, p, m_1, m_2) . \qquad \textbf{(IV-16)}$$

As in the case of a one-component system of one phase and of variable mass it is **known** from experiment that the entropy is an extensive function. Thus the total entropy is equal to the total mass times the specific entropy

$$S = (m_1 + m_2)\breve{S} \ . \qquad \text{(IV-17)}$$

Furthermore it is known that the specific entropy is a function of the absolute thermodynamic temperature, the pressure, and the mass fraction of component 1,

$$\breve{S} = \phi(T, p, \breve{m}_1) \ . \qquad \text{(IV-18)}$$

Thus the relation of the total entropy to the absolute thermodynamic temperature, the pressure, the mass of component 1, and the mass of component 2 is expressed by the equation

$$S(T, p, m_1, m_2) - S(T_0, p_0, m_{1_0}, m_{2_0})$$

$$= \int_{T_0, p_0, m_{1_0}, m_{2_0}}^{T, p, m_1, m_2} \left\{ (m_1 + m_2)\frac{\breve{c}_p}{T} dT + (m_1 + m_2)\frac{\breve{l}_p}{T} dp \right.$$

$$\left. + \frac{\partial S}{\partial m_1} dm_1 + \frac{\partial S}{\partial m_2} dm_2 \right\} . \qquad \text{(IV-19)}$$

From equations (IV-16), (IV-17), (IV-18), and (IV-19) it follows that

$$\left(\frac{\partial S}{\partial T}\right)_{p,\, m_1,\, m_2} = (m_1 + m_2)\frac{\breve{c}_p}{T}\,, \tag{IV-20}$$

$$\left(\frac{\partial S}{\partial p}\right)_{T,\, m_1,\, m_2} = (m_1 + m_2)\frac{\breve{l}_p}{T}\,, \tag{IV-21}$$

$$\left(\frac{\partial S}{\partial m_1}\right)_{T,\, p,\, m_2} = \breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\, p}\,, \tag{IV-22}$$

and

$$\left(\frac{\partial S}{\partial m_2}\right)_{T,\, p,\, m_1} = \breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\, p}\,. \tag{IV-23}$$

Necessary and sufficient conditions for (IV-11) are

$$\left\{\frac{\partial\left[(m_1 + m_2)\left(\breve{l}_p - p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1}\right)\right]}{\partial T}\right\}_{p,\, m_1,\, m_2}$$

$$= \left\{\frac{\partial\left[(m_1 + m_2)\left(\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1}\right)\right]}{\partial p}\right\}_{T,\, m_1,\, m_2}\,, \tag{IV-24}$$

$$\left\{\frac{\partial\left(\frac{\partial U}{\partial m_1}\right)_{T,p,m_2}}{\partial T}\right\}_{p,m_1,m_2} = \left\{\frac{\partial\left[(m_1+m_2)\left(\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\right)\right]}{\partial m_1}\right\}_{T,p,m_2}, \qquad \text{(IV-25)}$$

$$\left\{\frac{\partial\left(\frac{\partial U}{\partial m_2}\right)_{T,p,m_1}}{\partial T}\right\}_{p,m_1,m_2} = \left\{\frac{\partial\left[(m_1+m_2)\left(\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\right)\right]}{\partial m_2}\right\}_{T,p,m_1}, \qquad \text{(IV-26)}$$

$$\left\{\frac{\partial\left(\frac{\partial U}{\partial m_1}\right)_{T,p,m_2}}{\partial p}\right\}_{T,m_1,m_2} = \left\{\frac{\partial\left[(m_1+m_2)\left(\breve{l}_p - p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right)\right]}{\partial m_1}\right\}_{T,p,m_2}, \qquad \text{(IV-27)}$$

$$\left\{\frac{\partial\left(\frac{\partial U}{\partial m_2}\right)_{T,\,p,\,m_1}}{\partial p}\right\}_{T,\,m_1,\,m_2}$$

$$= \left\{\frac{\partial\left[(m_1 + m_2)\left(\breve{l}_p - p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,m_1}\right)\right]}{\partial m_2}\right\}_{T,\,p,\,m_1}, \qquad \text{(IV-28)}$$

and

$$\left\{\frac{\partial\left(\frac{\partial U}{\partial m_1}\right)_{T,\,p,\,m_2}}{\partial m_2}\right\}_{T,\,p,\,m_1} = \left\{\frac{\partial\left(\frac{\partial U}{\partial m_2}\right)_{T,\,p,\,m_1}}{\partial m_1}\right\}_{T,\,p,\,m_2}. \qquad \text{(IV-29)}$$

Similarly, necessary and sufficient conditions for (IV-19) are

$$\left\{\frac{\partial\left[(m_1 + m_2)\frac{\breve{l}_p}{T}\right]}{\partial T}\right\}_{p,\,m_1,\,m_2} = \left\{\frac{\partial\left[(m_1 + m_2)\frac{\breve{c}_p}{T}\right]}{\partial p}\right\}_{T,\,m_1,\,m_2}, \qquad \text{(IV-30)}$$

$$\left\{\frac{\partial\left(\frac{\partial S}{\partial m_1}\right)_{T,\,p,\,m_2}}{\partial T}\right\} = \left\{\frac{\partial\left[(m_1 + m_2)\frac{\breve{c}_p}{T}\right]}{\partial m_1}\right\}_{T,\,p,\,m_2}, \qquad \text{(IV-31)}$$

$$\left\{\frac{\partial\left(\frac{\partial S}{\partial m_2}\right)_{T,\,p,\,m_1}}{\partial T}\right\}_{p,\,m_1,\,m_2} = \left\{\frac{\partial\left[(m_1+m_2)\frac{\breve{c}_p}{T}\right]}{\partial m_2}\right\}_{T,\,p,\,m_1}, \quad \text{(IV-32)}$$

$$\left\{\frac{\partial\left(\frac{\partial S}{\partial m_1}\right)_{T,\,p,\,m_2}}{\partial p}\right\}_{T,\,m_1,\,m_2} = \left\{\frac{\partial\left[(m_1+m_2)\frac{\breve{l}_p}{T}\right]}{\partial m_1}\right\}_{T,\,p,\,m_2}, \quad \text{(IV-33)}$$

$$\left\{\frac{\partial\left(\frac{\partial S}{\partial m_2}\right)_{T,\,p,\,m_1}}{\partial p}\right\}_{T,\,m_1,\,m_2} = \left\{\frac{\partial\left[(m_1+m_2)\frac{\breve{l}_p}{T}\right]}{\partial m_2}\right\}_{T,\,p,\,m_1}, \quad \text{(IV-34)}$$

and

$$\left\{\frac{\partial\left(\frac{\partial S}{\partial m_1}\right)_{T,\,p,\,m_2}}{\partial m_2}\right\}_{T,\,p,\,m_1} = \left\{\frac{\partial\left(\frac{\partial S}{\partial m_2}\right)_{T,\,p,\,m_1}}{\partial m_1}\right\}_{T,\,p,\,m_2}. \quad \text{(IV-35)}$$

Carrying out the indicated differentiations in equation (IV-24) one has

$$(m_1+m_2)\left[\left(\frac{\partial \breve{l}_p}{\partial T}\right)_{p,\,m_1,\,m_2} - p\left(\frac{\partial\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}}{\partial T}\right)_{p,\,m_1,\,m_2}\right]$$

$$= (m_1+m_2)\left[\left(\frac{\partial \breve{c}_p}{\partial p}\right)_{T,\,m_1,\,m_2} - p\left(\frac{\partial\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}}{\partial p}\right)_{T,\,m_1,\,m_2} - \left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}\right].$$

(IV-36)

Making use of the change of variable theorem in partial differentiation one obtains

$$\left(\frac{\partial \breve{l}_p}{\partial T}\right)_{p,\, m_1,\, m_2} = \left(\frac{\partial \breve{l}_p}{\partial T}\right)_{p,\, \breve{m}_1} \left(\frac{\partial T}{\partial T}\right)_{p,\, m_1,\, m_2}$$

$$+ \left(\frac{\partial \breve{l}_p}{\partial p}\right)_{T,\, \breve{m}_1} \left(\frac{\partial p}{\partial T}\right)_{p,\, m_1,\, m_2} + \left(\frac{\partial \breve{l}_p}{\partial \breve{m}_1}\right)_{T,\, p} \left(\frac{\partial \breve{m}_1}{\partial T}\right)_{p,\, m_1,\, m_2} . \tag{IV-37}$$

The derivatives $\left(\frac{\partial p}{\partial T}\right)_{p,\, m_1,\, m_2}$ and $\left(\frac{\partial \breve{m}_1}{\partial T}\right)_{p,\, m_1,\, m_2}$ are each equal to zero. Thus one has

$$\left(\frac{\partial \breve{l}_p}{\partial T}\right)_{p,\, m_1,\, m_2} = \left(\frac{\partial \breve{l}_p}{\partial T}\right)_{p,\, \breve{m}_1} . \tag{IV-38}$$

Similarly it follows that

$$\left(\frac{\partial \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1}}{\partial T}\right)_{p,\, m_1,\, m_2} = \left(\frac{\partial \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1}}{\partial T}\right)_{p,\, \breve{m}_1} = \frac{\partial^2 \breve{V}}{\partial T \partial p} , \tag{IV-39}$$

also

$$\left(\frac{\partial \breve{c}_p}{\partial p}\right)_{T,\, m_1,\, m_2} = \left(\frac{\partial \breve{c}_p}{\partial p}\right)_{T,\, \breve{m}_1} \tag{IV-40}$$

and

$$\left(\frac{\partial\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}}{\partial p}\right)_{T,m_1,m_2} = \left(\frac{\partial\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}}{\partial p}\right)_{T,\breve{m}_1} = \frac{\partial^2 \breve{V}}{\partial p \partial T} . \tag{IV-41}$$

Consequently substituting the values of $\left(\frac{\partial \breve{H}}{\partial T}\right)_{p,m_1,m_2}$,

$$\left(\frac{\partial\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}}{\partial T}\right), \quad \left(\frac{\partial \breve{C}_p}{\partial p}\right)_{T,m_1,m_2}, \text{ and } \left(\frac{\partial\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}}{\partial p}\right)_{m}$$

from equations (IV-38), (IV-39), (IV-40), and (IV-41) in equation (IV-36) one obtains

$$\frac{\partial \breve{H}}{\partial T} - p\frac{\partial^2 \breve{V}}{\partial T \partial p} = \frac{\partial \breve{C}_p}{\partial p} - p\frac{\partial^2 \breve{V}}{\partial p \partial T} - \frac{\partial \breve{H}}{\partial T} . \tag{IV-42}$$

In a similar way carrying out the indicated differentiations in equation (IV-30) and making use of the change of variable theorem in partial differentiation one obtains

$$\frac{1}{} \ldots l_p \quad \frac{1}{T}\frac{\partial \breve{C}_p}{\partial p} . \tag{IV-43}$$

Combining equations (IV-42) and (IV-43) one has

$$\breve{c}_p = -T\,\frac{\partial \breve{K}}{\partial T}\,. \qquad \text{(IV-44)}$$

Carrying out the indicated differentiations in equation (IV-25) one has

$$\left(\frac{\partial\left(\frac{\partial U}{\partial m_1}\right)_{T,p,m_2}}{\partial T}\right)_{p,m_1,m_2} = (m_1+m_2)\left[\left(\frac{\partial \breve{c}_p}{\partial m_1}\right)_{T,p,m_2} - p\left(\frac{\partial\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}}{\partial m_1}\right)_{T,p,m_2}\right] + \breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\,. \qquad \text{(IV-45)}$$

Making use of equation (IV-14) one has

$$\left(\frac{\partial\left(\frac{\partial U}{\partial m_1}\right)_{T,p,m_2}}{\partial T}\right)_{p,m_1,m_2} = \left(\frac{\partial\left(\breve{U}+\breve{m}_2\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p}\right)}{\partial T}\right)_{p,m_1,m_2}$$

$$= \left(\frac{\partial \breve{U}}{\partial T}\right)_{p,m_1,m_2} + \breve{m}_2\left(\frac{\partial\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p}}{\partial T}\right)_{p,m_1,m_2}\,. \qquad \text{(IV-46)}$$

By application of the change of variable theorem in partial differentiation one then obtains

$$\left(\frac{\partial \breve{U}}{\partial T}\right)_{p,\, m_1,\, m_2} = \left(\frac{\partial \breve{U}}{\partial T}\right)_{p,\, \breve{m}_1} + \left(\frac{\partial \breve{U}}{\partial p}\right)_{T,\, \breve{m}_1}\left(\frac{\partial p}{\partial T}\right)_{p,\, m_1,\, m_2} + \left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\, p}\left(\frac{\partial \breve{m}_1}{\partial T}\right)_{p,\, m_1,\, m_2} . \tag{IV-47}$$

The derivatives $\left(\frac{\partial p}{\partial T}\right)_{p,\, m_1,\, m_2}$ and $\left(\frac{\partial \breve{m}_1}{\partial T}\right)_{p,\, m_1,\, m_2}$ are each equal to zero. Thus one has

$$\left(\frac{\partial \breve{U}}{\partial T}\right)_{p,\, m_1,\, m_2} = \left(\frac{\partial \breve{U}}{\partial T}\right)_{p,\, \breve{m}_1} . \tag{IV-48}$$

Similarly it follows that

$$\left(\frac{\partial \left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\, p}}{\partial T}\right)_{p,\, m_1,\, m_2} = \left(\frac{\partial \left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\, p}}{\partial T}\right)_{p,\, \breve{m}_1} = \frac{\partial^2 \breve{U}}{\partial T \partial \breve{m}_1} . \tag{IV-49}$$

Also by application of the change of variable theorem in partial differentiation one obtains

$$\left(\frac{\partial \breve{c}_p}{\partial m_1}\right)_{T,\,p,\,m_2} = \left(\frac{\partial \breve{c}_p}{\partial T}\right)_{p,\,\breve{m}_1}\left(\frac{\partial T}{\partial m_1}\right)_{T,\,p,\,m_2} + \left(\frac{\partial \breve{c}_p}{\partial p}\right)_{T,\,\breve{m}_1}\left(\frac{\partial p}{\partial m_1}\right)_{T,\,p,\,m_2} + \left(\frac{\partial \breve{c}_p}{\partial \breve{m}_1}\right)_{T,\,p}\left(\frac{\partial \breve{m}_1}{\partial m_1}\right)_{T,\,p,\,m_2} .$$

(IV-50)

The two derivatives $\left(\frac{\partial T}{\partial m_1}\right)_{T,\,p,\,m_2}$ and $\left(\frac{\partial p}{\partial m_1}\right)_{T,\,p,\,m_2}$ are each equal to zero and the derivative $\left(\frac{\partial \breve{m}_1}{\partial m_1}\right)_{T,\,p,\,m_2}$ is equal to $\frac{\breve{m}_2}{m_1 + m_2}$. Thus we have

$$\left(\frac{\partial \breve{c}_p}{\partial m_1}\right)_{T,\,p,\,m_2} = \left(\frac{\partial \breve{c}_p}{\partial \breve{m}_1}\right)_{T,\,p} \frac{\breve{m}_2}{m_1 + m_2} . \qquad \text{(IV-51)}$$

Similarly we have

$$\left(\frac{\partial\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}}{\partial m_1}\right)_{T,p,m_2} = \left(\frac{\partial\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}}{\partial \breve{m}_1}\right)_{T,p} \frac{\breve{m}_2}{m_1 + m_2}$$

$$= \frac{\partial^2 \breve{V}}{\partial \breve{m}_1 \partial T} \frac{\breve{m}_2}{m_1 + m_2}. \qquad \text{(IV-52)}$$

Consequently substituting the values of the derivatives from the right side of equation (IV-46) for the value of the derivative on the left side of equation (IV-45) one obtains

$$\left(\frac{\partial \breve{U}}{\partial T}\right)_{p,m_1,m_2} + \breve{m}_1\left(\frac{\partial\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p}}{\partial T}\right)_{p,m_1,m_2}$$

$$= (m_1 + m_2)\left[\left(\frac{\partial \breve{C}_p}{\partial m_1}\right)_{T,p,m_2} - p\left(\frac{\partial\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}}{\partial m_1}\right)_{T,p,m_2}\right]$$

$$+ \breve{C}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}. \qquad \text{(IV-53)}$$

Next substituting the values of the derivatives from equations (IV-48), (IV-49), (IV-51), and (IV-52) in equation (IV-53) one has

$$\left(\frac{\partial \breve{U}}{\partial T}\right)_{p,\breve{m}_1} + \breve{m}_2 \frac{\partial^2 \breve{U}}{\partial T \partial \breve{m}_1}$$

$$= (m_1 + m_2)\left[\frac{\breve{m}_2}{m_1 + m_2}\left(\frac{\partial \breve{c}_p}{\partial \breve{m}_1}\right)_{T,p} - \frac{\breve{m}_2}{m_1 + m_2}\, p\, \frac{\partial^2 \breve{V}}{\partial \breve{m}_1 \partial T}\right]$$

$$+ \breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right) . \qquad \text{(IV-54)}$$

The derivative $\left(\frac{\partial \breve{U}}{\partial T}\right)_{p,\breve{m}_1}$ is equal to $\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}$.

Hence one obtains finally

$$\frac{\partial^2 \breve{U}}{\partial T \partial \breve{m}_1} = \frac{\partial \breve{c}_p}{\partial \breve{m}_1} - p\frac{\partial^2 \breve{V}}{\partial \breve{m}_1 \partial T} \; [1] \qquad \text{(IV-55)}$$

In a similar way carrying out the indicated differentiations in equation (IV-31) and making use of the change of variable theorem in partial differentiation one has

M: - i -ssf- • [2] (IV-56)

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[1] The same result is derivable from equation (I¥-26)..

[2] The same result is derivable from equation **(IV-32).**

Combining equations (IV-55) and (IV-56) one has

$$\frac{\partial^2 \breve{U}}{\partial T \partial \breve{m}_1} = T \frac{\partial^2 \breve{S}}{\partial T \partial \breve{m}_1} - p \frac{\partial^2 \breve{V}}{\partial T \partial \breve{m}_1} \cdot \qquad \text{(IV-57)}$$

Likewise carrying out the indicated differentiations in equation (IV-27) and making use of the change of variable theorem in partial differentiation one obtains

$$\frac{\partial^2 \breve{U}}{\partial p \partial \breve{m}_1} \quad \partial \breve{p} \quad \partial^2 \breve{V} \qquad \text{(IV-58)}$$

Also, carrying out the indicated differentiations in equation (IV-33) and making use of the change of variable theorem in partial differentiation one has

$$\frac{\partial^2 \breve{S}}{\partial p \partial \breve{m}_1} = \frac{1}{T} \frac{\partial \breve{l}_p}{\partial \breve{m}_1} \cdot \qquad \text{(IV-59)}$$

Combining equations (IV-58) and (IV-59) one has

$$\frac{\partial^2 \breve{U}}{\partial p \partial \breve{m}_1} = T \frac{\partial^2 \breve{S}}{\partial p \partial \breve{m}_1} - p \frac{\partial^2 \breve{V}}{\partial p \partial \breve{m}_1} \cdot \qquad \text{(IV-60)}$$

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[3] The same result is derivable from equation (IV-28).

[4] The same result is derivable from equation (IV-34).

From (IV-44) it follows that

$$\frac{\partial \breve{l}_p}{\partial T} = -T\frac{\partial^2 \breve{V}}{\partial T^2} - \frac{\partial \breve{V}}{\partial T} \tag{IV-61}$$

and from (IV-43), (IV-44) and (IV-61) it also follows that

$$\frac{\partial \breve{c}_p}{\partial p} = -T\frac{\partial^2 \breve{V}}{\partial T^2} \ . \tag{IV-62}$$

From (IV-44) it follows that

$$\frac{\partial \breve{l}_p}{\partial p} = -T\frac{\partial^2 \breve{V}}{\partial p \partial T} \tag{IV-63}$$

and

$$\frac{\partial \breve{l}_p}{\partial \breve{m}_1} = -T\frac{\partial^2 \breve{V}}{\partial \breve{m}_1 \partial T} \ . \tag{IV-64}$$

Combining (IV-58) and (IV-64) one has

$$\frac{\text{[illegible]}}{\partial p \partial \breve{m}_1} = -T\frac{\text{[illegible]}}{\partial \breve{m}_1 \partial T} - \frac{\text{[illegible]}}{\partial \breve{m}_1 \partial p} \tag{IV-65}$$

and, similarly, combining **(IV-59)** and **(IV-64)** one has

$$\frac{\partial^2 \breve{S}}{\partial p \partial \breve{m}_1} = -\frac{\partial^2 \breve{V}}{\partial \breve{m}_1 \partial T} \ . \tag{IV-66}$$

Finally substituting the value of l_p from equation (IV-44) in equations (IV-13) and (IV-21) one obtains

$$\left(\frac{\partial U}{\partial p}\right)_{T,\, m_1,\, m_2} = -(m_1 + m_2)\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1} + p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1}\right] \tag{IV-67}$$

and

$$\left(\frac{\partial S}{\partial p}\right)_{T,\, m_1,\, m_2} = -(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1} . \tag{IV-68}$$

Thus, just as in the case of a binary system of one phase and of unit mass, there is one relation, equation (IV-44), between the seven derivatives, $\frac{\partial \breve{V}}{\partial T}$, $\frac{\partial \breve{V}}{\partial p}$, $\frac{\partial \breve{V}}{\partial \breve{m}_1}$, $\breve{c}_p$, $\breve{l}_p$, $\frac{\partial \breve{U}}{\partial \breve{m}_1}$, $\frac{\partial \breve{S}}{\partial \breve{m}_1}$. Consequently all seven will be known if the following six are determined by means of experimental measurements: $\frac{\partial \breve{V}}{\partial T}$, $\frac{\partial \breve{V}}{\partial p}$, $\frac{\partial \breve{V}}{\partial \breve{m}_1}$, $\breve{c}_p$, $\frac{\partial \breve{U}}{\partial \breve{m}_1}$, $\frac{\partial \breve{S}}{\partial \breve{m}_1}$. There are also eight relations, equations (IV-55), (IV-56), (IV-61), (IV-62), (IV-63), (IV-64), (IV-65), (IV-66), between the eighteen derivatives, $\frac{\partial^2 \breve{V}}{\partial T^2}$, $\frac{\partial^2 \breve{V}}{\partial p^2}$, $\frac{\partial^2 \breve{V}}{\partial \breve{m}_1^2}$, $\frac{\partial^2 \breve{V}}{\partial T \partial p}$, $\frac{\partial^2 \breve{V}}{\partial T \partial \breve{m}_1}$, $\frac{\partial^2 \breve{V}}{\partial p \partial \breve{m}_1}$,

$\frac{\partial \breve{c}_p}{\partial T}$, [illegible], [illegible], [illegible], [illegible], [illegible], $\frac{\partial^2 \breve{U}}{\partial T \partial \breve{m}_1}$, $\frac{\partial^2 \breve{U}}{\partial p \partial \breve{m}_1}$, $\frac{\partial^2 \breve{U}}{\partial \breve{m}_1^2}$,

$\frac{\partial^2 \breve{S}}{\partial T \partial \breve{m}_1}$, $\frac{\partial^2 \breve{S}}{\partial p \partial \breve{m}_1}$, $\frac{\partial^2 \breve{S}}{\partial \breve{m}_1^2}$, by means of which from the following ten,

$\frac{\partial^2 \breve{V}}{\partial T^2}$, $\frac{\partial^2 \breve{V}}{\partial p^2}$, $\frac{\partial^2 \breve{V}}{\partial \breve{m}_1^2}$, $\frac{\partial^2 \breve{V}}{\partial T \partial p}$, $\frac{\partial^2 \breve{V}}{\partial T \partial \breve{m}_1}$, $\frac{\partial^2 \breve{V}}{\partial p \partial \breve{m}_1}$, $\frac{\partial \breve{c}_p}{\partial T}$, $\frac{\partial \breve{c}_p}{\partial \breve{m}_1}$, $\frac{\partial^2 \breve{U}}{\partial \breve{m}_1^2}$, $\frac{\partial^2 \breve{S}}{\partial \breve{m}_1^2}$,

the remaining eight can be calculated. From equation (IV-62) $\frac{\partial \breve{c}_p}{\partial p}$ can be calculated; from equation (IV-61) [illegible] can be calculated; from equation (IV-63) [illegible] can be calculated; from equation (IV-64) [illegible] can be calculated; from equation (IV-55) $\frac{\partial^2 \breve{U}}{\partial T \partial \breve{m}_1}$ can be calculated; from equation (IV-55) $\frac{\partial^2 \breve{U}}{\partial p \partial \breve{m}_1}$ can be calculated; from equation (IV-56) $\frac{\partial^2 \breve{S}}{\partial T \partial \breve{m}_1}$ can be calculated; and from equation (IV-66) $\frac{\partial^2 \breve{S}}{\partial p \partial \breve{m}_1}$ can be calculated.

It will therefore suffice in the case of a binary system of one phase and of variable total mass, just as in the case of a binary system of one phase and of unit mass, to determine the specific volume over the range of temperature, pressure, and composition that is of interest. The value of $\breve{c}_p$ then needs to be determined as a function of temperature and composition at one pressure. Finally the values of the energy and the entropy need to be determined as functions of the composition at one temperature and one pressure. Thus in order to obtain complete therraodynamic information for a binary system of one phase and of variable total mass no additional experimental measurements have to be made beyond those required to be made in order to obtain complete thermodynamic information for a binary system of one phase and of unit mass over the same range of temperature, pressure, and composition. The necessary measurements to obtain complete thermodynamic information for a binary system of one phase and of unit mass over a given range of temperature, pressure, and composition were described in Part III of this text on pages 126-136. In part III the use of galvanic cells to determine the specific Gibbs function was explained, and from the specific Gibbs function combined with measurements of the specific volume and determinations of the specific energy (which do not require measurements of heat quantities under equilibrium conditions) the calculation of the specific entropy was also explained. In the author's article entitled "The Operational Basis and Mathematical Derivation of the Gibbs Differential Equation, Which Is the Fundamental Equation of Chemical Thermodynamics"[5] it was shown how osmotic cells could also be used in place of galvanic cells to obtain the specific Gibbs function.

It is notable that in order to obtain complete thermodynamic information for a binary system of one phase and of unit mass, and likewise for a binary system of one phase

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[5] Tunell, G., in *Thermodynamics of Minerals and Melts - Advances in Physical Geochemistry,* edited by R.C. Newton, A. Navrotsky, and 3.J. Wood, Springer-Verlag New York, Inc., New York, Heidelberg, Berlin, 1981, pp. 3-16.

and of variable total mass no definition or measurement of heat or work in the case of an open system when masses are being transferred to or from the system is required.[6]

Derivation of any desired relation between the thermodynamic quantities T, p, m_1, m_2, V, U, S, and their first derivatives for a binary system of one phase and of variable total mass by the use of functional determinants (Jacobians)

Equations (IV-1), (IV-11), and (IV-19) can, in general, be solved for any three of the quantities, T, p, m_1, m_2, V, U, S, as functions of the remaining four. The first partial derivative of any one of the quantities, T, p, m_1, m_2, V, U, S, with respect to any second quantity when any third, fourth, and fifth quantities are held constant can be obtained in terms of the six derivatives $\frac{\partial \breve{V}}{\partial T}$, $\frac{\partial \breve{V}}{\partial p}$, $\frac{\partial \breve{V}}{\partial \breve{m}_1}$, $\breve{c}_p$, $\frac{\partial \breve{U}}{\partial \breve{m}_1}$, $\frac{\partial \breve{S}}{\partial \breve{m}_1}$, and certain of the quantities T, p, m_1, m_2, $\breve{m}_1$, $\breve{m}_2$, $\breve{V}$, $\breve{U}$, $\breve{S}$, by application of the theorem stating that, if $w' = \psi(w, x, y, z)$, $w = f(s, t, u, v)$, $x = \phi(s, t, u, v)$, $y = \chi(s, t, u, v)$, $z = \theta(s, t, u, v)$, then one has

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[6] The definitions of heat and work in the case of open systems used by various authors are discussed in Appendix A to Part II and Appendix A to Part IV of this text.

$$\left(\frac{\partial w'}{\partial w}\right)_{x,\,y,\,z} = \frac{\begin{vmatrix} \frac{\partial w'}{\partial s} & \frac{\partial w'}{\partial t} & \frac{\partial w'}{\partial u} & \frac{\partial w'}{\partial v} \\ \frac{\partial x}{\partial s} & \frac{\partial x}{\partial t} & \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} \\ \frac{\partial y}{\partial s} & \frac{\partial y}{\partial t} & \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} \\ \frac{\partial z}{\partial s} & \frac{\partial z}{\partial t} & \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} \end{vmatrix}}{\begin{vmatrix} \frac{\partial w}{\partial s} & \frac{\partial w}{\partial t} & \frac{\partial w}{\partial u} & \frac{\partial w}{\partial v} \\ \frac{\partial x}{\partial s} & \frac{\partial x}{\partial t} & \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} \\ \frac{\partial y}{\partial s} & \frac{\partial y}{\partial t} & \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} \\ \frac{\partial z}{\partial s} & \frac{\partial z}{\partial t} & \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} \end{vmatrix}} = \frac{\dfrac{\partial(w',\,x,\,y,\,z)}{\partial(s,\,t,\,u,\,v)}}{\dfrac{\partial(w,\,x,\,y,\,z)}{\partial(s,\,t,\,u,\,v)}}, \qquad \text{(IV-69)}$$

provided all the partial derivatives are continuous and provided the determinant in the denominator is not equal to zero.

In Tables IV-1 to IV-35 (on pages 230-264) the value of the Jacobian is given for each set of four of the variables, T, p, [illegible] as w', x, y, z or w, x, y, z, and with T, p, m_1, m_2 as s, t, u, v. There are 140 Jacobians in the Tables, but one has

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

(IV-70), (IV-71), (IV-72)

because interchanging two rows of a determinant changes the sign of the determinant. Hence it is only necessary to calculate the values of 35 of the 140 Jacobians. The calculations of these 35 Jacobians follow:

$$\frac{\partial(m_2, T, p, m_1)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial m_2}{\partial T} \cdot 0 - \frac{\partial m_2}{\partial p} \cdot 0 + \frac{\partial m_2}{\partial m_1} \cdot 0 - \frac{\partial m_2}{\partial m_2} \cdot 1$$

$$= 0 - 0 + 0 - 1 \cdot 1$$

$$= -1 \; ; \qquad \text{(IV-73)}$$

$$\frac{\partial(V, T, p, m_1)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial V}{\partial T} \cdot 0 - \frac{\partial V}{\partial p} \cdot 0 + \frac{\partial V}{\partial m_1} \cdot 0 - \frac{\partial V}{\partial m_2} \cdot 1$$

$$= -\frac{\partial V}{\partial m_2}$$

$$= -\breve{V} + \breve{m}_1 \left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} ; \qquad \text{(IV-74)}$$

$$\frac{\partial(U, T, p, m_1)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \end{vmatrix}$$

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$$= -\frac{\partial U}{\partial m_2}$$

$$= -\breve{U} + \breve{m}_1\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} ; \qquad \text{(IV-75)}$$

$$\frac{\partial(S,\ T,\ p,\ m_1)}{\partial(T,\ p,\ m_1,\ m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T}\cdot 0 - \frac{\partial S}{\partial p}\cdot 0 + \frac{\partial S}{\partial m_1}\cdot 0 - \frac{\partial S}{\partial m_2}\cdot 1$$

$$= -\frac{\partial S}{\partial m_2}$$

$$= -\breve{S} + \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\ p}\ ; \qquad \text{(IV-76)}$$

$$\frac{\partial(V, T, p, \breve{m}_2)}{\partial(T, p, \breve{m}_1, \breve{m}_2)} = \begin{vmatrix} \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial V}{\partial T} \cdot 0 - \frac{\partial V}{\partial p} \cdot 0 + \quad \partial m_1 \qquad \partial m_2$$

$$= \frac{\partial V}{\partial m_1}$$

$$= \breve{V} + \breve{m}_2 \left(\frac{\partial \breve{V}}{\partial \breve{m}} \right)_{T, p} , \qquad \text{(IV-77)}$$

$$\frac{\partial(U,\ T,\ p,\ m_2)}{\partial(T,\ p,\ m_1,\ m_2)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial U}{\partial T} \cdot 0 - \frac{\partial U}{\partial p} \cdot 0 + \frac{\partial U}{\partial m_1} \cdot 1 - \frac{\partial U}{\partial m_2} \cdot 0$$

$$= \frac{\partial U}{\partial m_1}$$

$$= \breve{U} + \breve{m}_2\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\ p}\ ; \qquad \text{(IV-78)}$$

$$\frac{\partial(S, T, p, m_2)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T} \cdot 0 - \frac{\partial S}{\partial p} \cdot 0 + \frac{\partial S}{\partial m_1} \cdot 1 - \frac{\partial S}{\partial m_2} \cdot 0$$

$$= \frac{\partial S}{\partial m_1}$$

$$= \bar{S}_1 \equiv \left(\frac{\partial S}{\partial m_1}\right)_{T, p} ; \qquad \text{(IV-79)}$$

$$\frac{\partial(U, T, p, V)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial U}{\partial T} \cdot 0 - \frac{\partial U}{\partial p} \cdot 0 + \frac{\partial U}{\partial m_1} \cdot \frac{\partial V}{\partial m_2} - \frac{\partial U}{\partial m_2} \cdot \frac{\partial V}{\partial m_1}$$

$$= \frac{\partial U}{\partial m_1} \frac{\partial V}{\partial m_2} - \frac{\partial U}{\partial m_2} \cdot \frac{\partial V}{\partial m_1}$$

$$= -\breve{U}\left(\frac{\partial \breve{V}}{\partial m_1}\right)_{T,\,p} + \breve{V}\left(\frac{\partial \breve{U}}{\partial m_1}\right)_{T,\,p} ; \qquad \text{(IV-80)}$$

$$\frac{\partial(S, T, p, V)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T} \cdot 0 - \frac{\partial S}{\partial p} \cdot 0 + \frac{\partial S}{\partial m_1}\frac{\partial V}{\partial m_2} - \frac{\partial S}{\partial m_2}\frac{\partial V}{\partial m_1}$$

$$= \frac{\partial S}{\partial m_1} \cdot \frac{\partial V}{\partial m_2} - \frac{\partial S}{\partial m_2} \cdot \frac{\partial V}{\partial m_1}$$

$$= -\breve{S}\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} + \breve{V}\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p} ; \qquad \text{(IV-81)}$$

$$\frac{\partial(S, T, p, U)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \end{vmatrix}$$

$$= \quad \partial T \quad \partial p \cdot 0 + \partial m_1 \quad \partial m_2 \quad \partial m_2 \quad \partial m_1$$

$$= \frac{\partial S}{\partial m_1} \cdot \frac{\partial U}{\partial m_2} - \frac{\partial S}{\partial m_2} \cdot \frac{\partial U}{\partial m_1}$$

$$= -\breve{S}\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + \breve{U}\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p} ; \qquad \text{(IV-82)}$$

$$\frac{\partial(V, T, m_1, m_2)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \end{vmatrix}$$

$$= \quad \frac{\partial V}{\partial T} \quad \frac{\partial V}{\partial p} \quad \frac{\partial V}{\partial m_1} \quad \frac{\partial V}{\partial m_2}$$

$$= - \frac{\partial V}{\partial p}$$

$$= -(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1}; \qquad \text{(IV-83)}$$

$$\frac{\partial(U,\ T,\ m_1,\ m_2)}{\partial(T,\ p,\ m_1,\ m_2)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial U}{\partial T}\cdot 0 - \frac{\partial U}{\partial p}\cdot 1 + \frac{\partial U}{\partial m_1}\cdot 0 - \frac{\partial U}{\partial m_2}\cdot 0$$

$$= -\frac{\partial U}{\partial p}$$

$$= (m_1 + m_2)\left[T\left(\frac{\partial \breve{v}}{\partial T}\right)_{p,\ \breve{m}_1} + p\left(\frac{\partial \breve{v}}{\partial p}\right)_{T,\ \breve{m}_1}\right]; \quad \text{(IV-84)}$$

$$\frac{\partial(S, T, m_1, m_2)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T} \cdot 0 - \frac{\partial S}{\partial p} \cdot 1 + \frac{\partial S}{\partial m_1} \cdot 0 - \frac{\partial S}{\partial m_2} \cdot 0$$

$$= -\frac{\partial S}{\partial p}$$

$$= (m_1 + m_2)\left(\frac{\partial \bar{V}}{\partial T}\right)_{p, \bar{m}_1}; \qquad \text{(IV-85)}$$

$$\frac{\partial(U,\ T,\ m_1,\ V)}{\partial(T,\ p,\ m_1,\ m_2)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial U}{\partial T} \cdot 0 - \frac{\partial U}{\partial p} \cdot \frac{\partial V}{\partial m_2} + \frac{\partial U}{\partial m_1} \cdot 0 + \frac{\partial U}{\partial m_2} \cdot \frac{\partial V}{\partial p}$$

$$= - \frac{\partial U}{\partial p} \cdot \frac{\partial V}{\partial m_2} + \frac{\partial U}{\partial m_1} \cdot \frac{\partial V}{\partial p}$$

$$= (m_1 + m_2)\left\{\left[(\breve{U} + p\breve{V}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\ p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\ p}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\ m_1}\right.$$

$$\left. + \left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\ p}\right] T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\ m_1}\right\}; \qquad \text{(IV-86)}$$

$$\frac{\partial(S, T, m_1, V)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T} \cdot 0 - \frac{\partial S}{\partial p} \cdot \frac{\partial V}{\partial m_2} + \frac{\partial S}{\partial m_1} \cdot 0 + \frac{\partial S}{\partial m_2} \cdot \frac{\partial V}{\partial p}$$

$$= -\frac{\partial S}{\partial p} \frac{\partial V}{\partial m_2} + \frac{\partial S}{\partial m_2} \frac{\partial V}{\partial p}$$

$$= (m_1 + m_2)\left\{\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\, p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1}\right.$$

$$\left. + \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\, p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1}\right\} ; \qquad \text{(IV-87)}$$

$$\frac{\partial(S,\ T,\ m_1,\ U)}{\partial(T,\ p,\ m_1,\ m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \end{vmatrix}$$

= dT dp dm 2 dm 1 dm 2 dp

= - i£ . ML + ML . ML
op dm 2 dm 2 dp

$$= (m_1 + m_2)\left\{\left[(\breve{U} - T\breve{S}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\ p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\ p}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\ \breve{m}_1}\right.$$

$$\left. - \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\ p}\right]p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\ \breve{m}_1}\right\} ; \qquad \text{(IV-88)}$$

$$\frac{\partial(U, T, m_2, V)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial U}{\partial T} \cdot 0 + \frac{\partial U}{\partial p} \cdot \frac{\partial V}{\partial m_1} - \frac{\partial U}{\partial m_1} \frac{\partial V}{\partial p} - \frac{\partial U}{\partial m_2} \cdot 0$$

$$= \frac{\partial U}{\partial p} \cdot \frac{\partial V}{\partial m_1} - \frac{\partial U}{\partial m_1} \cdot \frac{\partial V}{\partial p}$$

$$= -(m_1 + m_2)\left\{\left[(\breve{U} + p\breve{V}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right.$$

$$\left. + \left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right] T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\right\} ; \qquad \text{(IV-89)}$$

$$\frac{\partial(S,\ T,\ m_2,\ V)}{\partial(T,\ p,\ m_1,\ m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T} \cdot 0 + \frac{\partial S}{\partial p} \cdot \frac{\partial V}{\partial m_1} - \frac{\partial S}{\partial m_1} \cdot \frac{\partial V}{\partial p} - \frac{\partial S}{\partial m_2} \cdot 0$$

$$= \frac{\partial S}{\partial p} \cdot \frac{\partial V}{\partial m_1} - \frac{\partial S}{\partial m_1} \cdot \frac{\partial V}{\partial p}$$

$$= -(m_1 + m_2)\left\{\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\ p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\ \breve{m}_1}\right.$$

$$\left. + \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\ p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\ \breve{m}_1}\right\}. \qquad \textbf{(IV-90)}$$

$$\frac{\partial(S, T, m_2, U)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T} \cdot 0 + \frac{\partial S}{\partial p} \cdot \frac{\partial U}{\partial m_1} - \frac{\partial S}{\partial m_1} \frac{\partial U}{\partial p} - \frac{\partial S}{\partial m_2} \cdot 0$$

$$= \frac{\partial S}{\partial p} \cdot \frac{\partial U}{\partial m_1} - \frac{\partial S}{\partial m_1} \frac{\partial U}{\partial p}$$

$$= -(m_1 + m_2)\left\{\left[(\breve{U} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}\right.$$

$$\left. - \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p}\right] p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right\} ; \qquad \text{(IV-91)}$$

$$\frac{\partial(S,T,V,U)}{\partial(T,p,m_1,m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T}\cdot 0 - \frac{\partial S}{\partial p}\left(\frac{\partial V}{\partial m_1}\cdot\frac{\partial U}{\partial m_2} - \frac{\partial U}{\partial m_1}\cdot\frac{\partial V}{\partial m_2}\right)$$

$$+ \frac{\partial S}{\partial m_1}\left(\frac{\partial V}{\partial p}\cdot\frac{\partial U}{\partial m_2} - \frac{\partial U}{\partial p}\cdot\frac{\partial V}{\partial m_2}\right)$$

$$- \frac{\partial S}{\partial m_2}\left(\frac{\partial V}{\partial p}\cdot\frac{\partial U}{\partial m_1} - \frac{\partial U}{\partial p}\cdot\frac{\partial V}{\partial m_1}\right)$$

$$= (m_1 + m_2)\left\{\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - \breve{V}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\right.$$

$$\left. + \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p} - \breve{S}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\right\};$$

(IV-92)

$$\frac{\partial(V,\, p,\, m_1,\, m_2)}{\partial(T,\, p,\, m_1,\, m_2)} = \begin{vmatrix} \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial V}{\partial T} \cdot 1 - \frac{\partial V}{\partial p} \cdot 0 + \frac{\partial V}{\partial m_1} \cdot 0 - \frac{\partial V}{\partial m_2} \cdot 0$$

$$= \frac{\partial V}{\partial T}$$

$$= (m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1} ; \qquad \text{(IV-93)}$$

$$\frac{\partial(U, p, m_1, m_2)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial U}{\partial T} \cdot 1 - \frac{\partial U}{\partial p} \times 0 + \frac{\partial U}{\partial m_1} \cdot 0 - \frac{\partial U}{\partial m_2} \cdot 0$$

$$= \frac{\partial U}{\partial T}$$

$$= (m_1 + m_2)\left[\breve{c}_p - p\left(\frac{\partial \breve{v}}{\partial T}\right)_{p,\breve{m}_1}\right]; \qquad \text{(IV-94)}$$

$$\frac{\partial(S,\ p,\ m_1,\ m_2)}{\partial(T,\ p,\ m_1,\ m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T}\,\frac{\partial p}{\partial p}\,\frac{\partial m_1}{\partial m_1}\,\frac{\partial m_2}{\partial m_2}$$

$$= \frac{\partial S}{\partial T}$$

$$= (m_1 + m_2)\frac{c_p}{T} \; ; \qquad \text{(IV-95)}$$

$$\frac{\partial(U,\ p,\ m_1,\ V)}{\partial(T,\ p,\ m_1,\ m_2)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial U}{\partial T}\cdot\frac{\partial V}{\partial m_2} - \frac{\partial U}{\partial p}\cdot 0 + \frac{\partial U}{\partial m_1}\cdot 0 - \frac{\partial U}{\partial m_2}\cdot\frac{\partial V}{\partial T}$$

$$= \frac{\partial U}{\partial T}\cdot\frac{\partial V}{\partial m_2} - \frac{\partial U}{\partial m_2}\cdot\frac{\partial V}{\partial T}$$

$$= -(m_1 + m_2)\left\{\left[(\breve{U} + p\breve{V}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\ p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\ p}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\ \breve{m}_1}\right.$$

$$\left. - \breve{c}_p\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\ p}\right]\right\}; \qquad \text{(IV-96)}$$

$$\frac{\partial(S, p, m_1, V)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T} \cdot \frac{\partial V}{\partial m_2} - \frac{\partial S}{\partial p} \cdot 0 + \frac{\partial S}{\partial m_1} \cdot 0 - \frac{\partial S}{\partial m_2} \cdot \frac{\partial V}{\partial T}$$

$$= \frac{\partial S}{\partial T} \cdot \frac{\partial V}{\partial m_2} - \frac{\partial S}{\partial m_2} \cdot \frac{\partial V}{\partial T}$$

$$= (m_1 + m_2)\left\{\frac{\breve{c}_p}{T}\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\, p}\right] - \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\, p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1}\right\} ; \qquad \text{(IV-97)}$$

$$\frac{\partial(S, p, m_1, U)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T} \cdot \frac{\partial U}{\partial m_2} - \frac{\partial S}{\partial p} \cdot 0 + \frac{\partial S}{\partial m_1} \cdot 0 - \frac{\partial S}{\partial m_2} \cdot \frac{\partial U}{\partial T}$$

$$= \frac{\partial S}{\partial T} \cdot \frac{\partial U}{\partial m_2} - \frac{\partial S}{\partial m_2} \cdot \frac{\partial U}{\partial T}$$

$$= (m_1 + m_2)^{-1} \Bigg\{ \left[(\breve{U} - T\breve{S}) - \breve{m}_1 \left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1} \right)_{T,p} - T \left(\frac{\partial \breve{S}}{\partial \breve{m}_1} \right)_{T,p} \right) \right]$$

$$+ \left[\breve{S} - \breve{m}_1 \left(\frac{\partial \breve{S}}{\partial \breve{m}_1} \right)_{T,p} \right] p \left(\frac{\partial \breve{V}}{\partial T} \right)_{p, \breve{m}_1} \Bigg\} \; ; \qquad \text{(IV-98)}$$

$$\frac{\partial(U,\, p,\, m_2,\, V)}{\partial(T,\, p,\, m_1,\, m_2)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= -\frac{\partial U}{\partial T} \cdot \frac{\partial V}{\partial m_1} - \frac{\partial U}{\partial p} \cdot 0 + \frac{\partial U}{\partial m_1} \cdot \frac{\partial V}{\partial T} - \frac{\partial U}{\partial m_2} \cdot 0$$

$$= -\frac{\partial U}{\partial T} \cdot \frac{\partial V}{\partial m_1} + \frac{\partial U}{\partial m_1} \cdot \frac{\partial V}{\partial T}$$

$$= (m_1 + m_2)\left\{\left[(\breve{U} + p\breve{V}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}\right.$$

$$\left. - \breve{C}_p\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}\right]\right\} ; \qquad \text{(IV-99)}$$

$$\frac{\partial(S,\ p,\ m_2,\ V)}{\partial(T,\ p,\ m_1,\ m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= -\frac{\partial S}{\partial T}\cdot\frac{\partial V}{\partial m_1} - \frac{\partial S}{\partial p}\cdot 0 + \frac{\partial S}{\partial m_1}\cdot\frac{\partial V}{\partial T} - \frac{\partial S}{\partial m_2}\cdot 0$$

$$= -\frac{\partial S}{\partial T}\cdot\frac{\partial V}{\partial m_1} + \frac{\partial S}{\partial m_1}\cdot\frac{\partial V}{\partial T}$$

$$= -(m_1 + m_2)\left\{\frac{\breve{c}_p}{T}\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\ p}\right]\right.$$

$$\left. - \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\ p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\ \breve{m}_1}\right\} ; \qquad \text{(IV-100)}$$

$$\frac{\partial(S,\ p,\ m_2,\ U)}{\partial(T,\ p,\ m_1,\ m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \end{vmatrix}$$

$$= -\frac{\partial S}{\partial T}\cdot\frac{\partial U}{\partial m_1} - \frac{\partial S}{\partial p}\cdot 0 + \frac{\partial S}{\partial m_1}\cdot\frac{\partial U}{\partial T} - \frac{\partial S}{\partial m_2}\cdot 0$$

$$= -\frac{\partial S}{\partial T}\cdot\frac{\partial U}{\partial m_1} + \frac{\partial S}{\partial m_1}\cdot\frac{\partial U}{\partial T}$$

$$= -(m_1 + m_2)\left\{\frac{\breve{c}_p}{T}\left[(\breve{U} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\ p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\ p}\right)\right]\right.$$

$$\left. + \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\ p}\right] p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\ \breve{m}_1}\right\}\ ; \qquad \text{(IV-101)}$$

$$\frac{\partial(S,p,V,U)}{\partial(T,p,m_1,m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T}\left(\frac{\partial V}{\partial m_1} \cdot \frac{\partial U}{\partial m_2} - \frac{\partial U}{\partial m_1} \cdot \frac{\partial V}{\partial m_2}\right) - \frac{\partial S}{\partial p} \cdot 0$$

$$+ \frac{\partial S}{\partial m_1}\left(\frac{\partial V}{\partial m_2} \cdot \frac{\partial U}{\partial T} - \frac{\partial V}{\partial T} \cdot \frac{\partial U}{\partial m_2}\right)$$

$$- \frac{\partial S}{\partial m_2}\left(\frac{\partial V}{\partial m_1} \cdot \frac{\partial U}{\partial T} - \frac{\partial V}{\partial T} \cdot \frac{\partial U}{\partial m_1}\right)$$

$$(m_1 + m_2)\left\{\frac{\breve{c}_p}{T}\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p} - \breve{V}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p}\right)\right]\right.$$

$$\left. - \left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p} - \breve{S}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}\right)\right]\right\};$$

(IV-102)

$$\frac{\partial(U, m_1, m_2, V)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

= ML/3T * £L/3p " -3£/dp ' II/dT + 1^./3m/ n - 1^./3m2* n

= dT ' d p d p ' dT

$$= (m_1 + m_2)^2 \left[T \left(\frac{\partial \breve{V}}{\partial T} \right)^2_{p, \breve{m}_1} + \breve{c}_p \left(\frac{\partial \breve{V}}{\partial p} \right)_{T, \breve{m}_1} \right] ; \qquad \text{(IV-103)}$$

$$\frac{\partial(S, m_1, m_2, V)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T}\frac{\partial V}{\partial p} - \frac{\partial S}{\partial p}\frac{\partial V}{\partial T} + \frac{\partial S}{\partial m_1} 0 - \frac{\partial S}{\partial m_2} 0$$

$$= (m_1 + m_2)^2\left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\,\breve{m}_1} + \frac{\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right] \; ; \qquad \text{(IV-104)}$$

$$\frac{\partial(S, m_1, m_2, V)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T}\frac{\partial V}{\partial p} - \frac{\partial S}{\partial p}\frac{\partial V}{\partial T} + \frac{\partial S}{\partial m_1} \cdot 0 + \frac{\partial S}{\partial m_2} \cdot 0$$

$$= -(m_1 + m_2)^2 \left[p\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} + \frac{p\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1} \right] \quad ; \quad \text{(IV-105)}$$

$$\frac{\partial(S, m_1, V, U)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T}\left(\frac{\partial V}{\partial m_2} \cdot \frac{\partial U}{\partial p} - \frac{\partial V}{\partial p} \cdot \frac{\partial U}{\partial m_2}\right)$$

$$- \frac{\partial S}{\partial p}\left(\frac{\partial V}{\partial m_2} \cdot \frac{\partial U}{\partial T} - \frac{\partial V}{\partial T} \cdot \frac{\partial U}{\partial m_2}\right)$$

$$- \frac{\partial S}{\partial m_2}\left(\frac{\partial U}{\partial p} \cdot \frac{\partial V}{\partial T} - \frac{\partial V}{\partial p} \cdot \frac{\partial U}{\partial T}\right)$$

$$= -(m_1 + m_2)^2 \left\{\left[(\breve{U} + p\breve{V} - T\breve{S}) - \left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]\right.$$

$$\left. \cdot \left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} + \frac{\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right]\right\}; \qquad \text{(IV-106)}$$

$$\frac{\partial(S, m_2, V, U)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T}\left(\frac{\partial V}{\partial m_1}\frac{\partial U}{\partial p} - \frac{\partial U}{\partial m_1}\frac{\partial V}{\partial p}\right)$$

$$- \frac{\partial S}{\partial p}\left(\frac{\partial V}{\partial m_1}\frac{\partial U}{\partial T} - \frac{\partial U}{\partial m_1}\frac{\partial V}{\partial T}\right)$$

$$+ \frac{\partial S}{\partial m_1}\left(\frac{\partial V}{\partial p}\frac{\partial U}{\partial T} - \frac{\partial V}{\partial T}\frac{\partial U}{\partial p}\right) - \frac{\partial S}{\partial m_2}\cdot 0$$

$$= (m_1 + m_2)^2\left\{\left[(\breve{U} + p\breve{V} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\right.$$

$$\left.\cdot\left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right]\right\} . \qquad \text{(IV-107)}$$

Table IV-1
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(W, X, Y, Z)}{\partial(T, p, m_1, m_2)} = \frac{\partial(W, X, Y, Z)}{\partial(T, p, \breve{m}_1, \breve{m}_2)}$$

X, Y, Z / W	$T, p, \breve{m}_1$
02	-1
y	$-\breve{V} + \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}$
V	$-\breve{U} + \breve{m}_1\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p}$
S	$-\breve{S} + \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}$

Table IV-2
Jacobians of extensive functions for a
binary system of one phase

$$\frac{\partial(w', x, y, z)}{\text{O\l f P 1 Ul\i Ū12)}} \qquad \frac{\partial(w, x, y, z)}{\text{0\{i \$ pi El I f 1112)}}$$

\>r, y, z / w\ w \	**Ttp,** m_2
m_1	1
V	$\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}$
U	$\breve{U} + \breve{m}_2\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p}$
5	$\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}$

Table IV-3
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(V, x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(\breve{V}, x, y, z)}{\partial(T, p, \breve{m}_1, \breve{m}_2)}$$

x, y, z \ w	T, p, V
m_1	$\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}$
m_2	$-\breve{V} - \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}$
U	$-\breve{U}\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} + \breve{V}\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p}$
S	$-\breve{S}\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} + \breve{V}\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}$

Table IV-4
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)} = \frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}$$

x, y, z / w'	$T, p, \breve{U}$
m_1	[illegible] $\left(\frac{\partial \breve{U}}{\partial m_1}\right)_{T,p}$
m_2	$-\breve{U} - m_2\left(\frac{\partial \breve{U}}{\partial m_1}\right)_{T,p}$
V	$\breve{U}\left(\frac{\partial \breve{V}}{\partial m_1}\right)_{T,p} - \breve{V}\left(\frac{\partial \breve{U}}{\partial m_1}\right)_{T,p}$
S	$-\breve{S}\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + \breve{U}\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}$

Table IV-5
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)} \quad , \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

x, y, z / w', w	T, p, S
m_1	$\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}$
m_2	$-\breve{S} - \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}$
V	$\breve{S}\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - \breve{V}\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}$
U	$\breve{S}\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} - \breve{U}\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}$

Table IV-5
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)} \div \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

w' \ w ; x, y, z	T, m_1, m_2
p	-1
V	$-(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$
U	$(m_1 + m_2)\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} + p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right]$
S	$(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}$

Table IV-7
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w,\, x,\, y,\, z)}{\partial(T,\, p,\, m_1,\, m_2)}\ ,\qquad \frac{\partial(w,\, x,\, y,\, z)}{\partial(T,\, p,\, \breve{m}_1,\, m_2)}$$

x, y, z / w	$T,\ m_1,\ V$
p	$-\breve{V} + \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}$
[illegible]	$(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}$
V	$(m_1+m_2)\left\{\left[\breve{U} + p\breve{V} - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}\right)\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1} + \left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}\right]T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}\right\}$
S	$(m_1+m_2)\left\{\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1} + \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right\}$

Table IV-8
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

x, y, z → / w', w ↓	$T, m_1, \breve{U}$
p	$-\breve{U} + \breve{m}_1\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p}$
^2	$-(m_1 + m_2)\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} + p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right]$
>	-(mi + i33₂)|[(£1 + pV̆) - m̆ .//3ff \ /'®.)r.J(«l.Sl }
S	(mi + ffl₂)s{[(Lf - fe) - a•<(Ĭ,)T, p -nwr(PjjujP>ffi - KsJT .r, ˘aj

Table IV-9
Jacobians of extensive functions for a binary system of one phase

$\frac{\partial(x, y, z)}{\partial(T, p, m_1, m_2)}$; $\frac{\partial(x, y, z)}{\partial(T, p, m_1, m_2)}$	
x, y, z	T, m_1, S
P	$-\breve{S} + \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}$
[illegible]	$-(m_1 + m_2)\left(\frac{\partial V}{\partial T}\right)_{p, \breve{m}_1}$
V	$-(m_1 + m_2)\left\{\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\right.$ $\left.\left[\text{[illegible]} \left(\frac{\partial \text{[illegible]}}{\partial m_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right\}$
U	$-(m_1 + m_2)\left\{\left[(\breve{U} - T\breve{S}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\right.$ $\left. - \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right]p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right\}$

Table IV-10
Jacobians of extensive functions for a binary system of one phase

	$\frac{d(w^r, x, y, z)}{3(Tt\ pi\ E2\backslash *\ \hat{}2)}$ ' $\frac{d(w, x_f\ y, z)}{3(T^{**}\ p\text{»}\ /n1,\ m_2)}$
x, y, z ; w	r, m_2, V
P	7 •*•(&>„
·,	$-(\breve{m}_1 + \breve{m}_2)\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$
u	$+ p\breve{V}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,}\right.$ Mi, $+ \left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right] T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\}$
S	$-(\breve{m}_1 + \breve{m}_2)\left\{\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,}\right]\right.$ (M.) $+ \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\}$

Table IV-11
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}\ ,\qquad \frac{\partial(w, x, y, z)}{\partial(T, p, \breve{m}_1, \breve{m}_2)}$$

w' / w \ x, y, z	T, m_2, U
p	$\breve{U} + \breve{m}_2\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p}$
[illegible]	$(m_1 + m_2)\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1} + p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right]$
V	$(m_1 + m_2)\left\{\left[(\breve{U} + p\breve{V}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1} + \left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right]T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\right\}$
[illegible]	[illegible] $- T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1} - \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right\}$

Table IV-12
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

w', w \ x, y, z	T, m_2, S
p	$\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}$
[illegible]	$(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}$
V	$(m_1 + m_2)\left\{\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right]$ [illegible] $+ \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right\}$
[illegible]	[illegible] $T\breve{S}$ [illegible] $- T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}$ [illegible] $_{,\breve{m}_1}\right\}$

Table IV-13
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

w', w \ x, y, z	T, V, U
p	$-\breve{U}\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} + \breve{V}\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p}$
m_1	$(m_1 + m_2)\left\{\left[(\breve{U} + p\breve{V}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right.$ [illegible]
[illegible]	[illegible]
S	$(m_1 + m_2)\left\{\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - \breve{V}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\right.$ [illegible]

Table IV-14
Jacobians of extensive functions for a
binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, \breve{m}_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, \breve{m}_1, m_2)}$$

w \ x, y, z	T, V, S
p	$-\breve{S}\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} + \breve{V}\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}$
m_1	$(m_1 + m_2)\left\{\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} + \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right\}$
m_2	$-(m_1 + m_2)\left\{\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} + \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right\}$
U	$-(m_1 + m_2)\left\{\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} - \breve{V}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right)\right] + \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p} - \breve{S}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right)\right]\right\}$

Table IV-15
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}, \qquad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

x, y, z / w', w	T, U, S
p	$-\breve{S}\left(\frac{\partial \breve{U}}{\partial \breve{m}}\right)$ [illegible]
m_1	[illegible] $- T\breve{S}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p}$ [illegible] $- \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right] p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right\}$
m_2	$-(m_1 + m_2)\left\{\left[(\breve{U} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} - \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right] p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right\}$
V	$(m_1 + m_2)\left\{\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} - \breve{V}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right)\right] + \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p} - \breve{S}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right)\right]\right\}$

Table IV-16
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

w', w \ x, y, z	p, m_1, m_2
T	1
V	$(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial T}\right)_{\breve{m}_1}$
U	$(m_1 + m_2)\left[\breve{C}_p - p\left(\frac{\partial}{\partial} \ldots\right)\right]$
S	$(m_1 + m_2)\frac{\breve{C}_p}{T}$

Table IV-17
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, \breve{m}_1, \breve{m}_2)} * \frac{\partial(w, x, y, z)}{\partial(T, p, \breve{m}_1, \breve{m}_2)}$$

w' \ x, y, z	p. an V
T	$\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}$
m_2	… $+ m_2)\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}$
U	… $+ p\breve{V}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right)\Big]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}$ … $- \breve{c}_p^* \left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\Big\}$
S	$(m_1 + m_2)\left\{\frac{\breve{c}_p}{T}\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\right.$ $- \Big[$ S - ^i (-rt?) $\Big]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\Big\}$

Table IV-18
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)} = \frac{\partial(w, x, y, z)}{\partial(T, p, \breve{m}_1, m_2)}$$

w', w \ x, y, z	$p, \breve{m}_1, U$
T	$\breve{U} - \breve{m}_1\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\, p}$
m_2	$-(m_1 + m_2)\left[\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1}\right]$
V	$(m_1 + m_2)\left\{\left[(\breve{U} + p\breve{V}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\, p}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1} - \breve{c}_p\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\, p}\right]\right\}$
S	$(m_1 + m_2)\left\{\frac{\breve{c}_p}{T}\left[(\breve{U} - T\breve{S}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\, p}\right)\right] + \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\, p}\right]p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1}\right\}$

Table IV-19 Jacobians of extensive functions for a binary system of one phase	
$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}$, $\frac{\partial(w, x, y, z)}{\partial(T, p, \breve{m}_1, \breve{m}_2)}$	
x, y, z \ w', w	p» i27 1» S
T	[illegible]
S	$-(m_1 + m_2)\frac{\breve{C}_p}{T}$
V	$-(m_1 + m_2)\left\{\frac{\breve{C}_p}{T}\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right] - \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\right\}$
U	$-(m_1 + m_2)\left\{\frac{\breve{C}_p}{T}\left[(\breve{U} - T\breve{S}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right)\right] + \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right]p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\right\}$

Table IV-20
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

x, y, z / w	p, m_2, V
T	$\breve{V} - \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}$
m_1	$(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}$
U	$+ p\breve{V}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right)\Big]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}$ $\ldots \breve{c}_p\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\Big\}$
S	$-(m_1 + m_2)\Big\{\frac{\breve{c}_p}{T}\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]$ $- \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\Big\}$

Table IV-21
Jacobians of extensive functions for a binary systen of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

x, y, z / w', w	p, m_1, U
T	$-\breve{U} - \breve{m}_2\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p}$
m_1	$(m_1 + m_2)\left[\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\right]$
V	$-(m_1 + m_2)\left\{\left[(\breve{U} + p\breve{V}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} - \breve{c}_p\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right]\right\}$
S	$-(m_1 + m_2)\left\{\frac{\breve{c}_p}{T}\left[(\breve{U} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right] + \left[\breve{S}\ \text{[illegible]}\right]_{p, \breve{m}_1}\right\}$

Table IV-22
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

w \ x, y, z	$p, \ldots, S$
T	$-\breve{S} - \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}$
m_1	$(m_1 + m_2)\frac{\breve{c}_p}{T}$
V	$(m_1 + m_2)\left\{\frac{\breve{c}_p}{T}\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right] - \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\right\}$
U	$(m_1 + m_2)\left\{\frac{\breve{c}_p}{T}\left[(\breve{U} - T\breve{S}) + \breve{m}_2\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p}\right] + \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\right\}$

Table IV-23
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)} \qquad \frac{\partial(w, x, y, z)}{[illegible]}$$

w \ x, y, z	$p, \breve{V}, U$
T	[illegible]
m_1	$-(m_1+m_2)\left\{\left[(\breve{U}+p\breve{V})-\breve{m}_1\left(\left(\frac{\partial\breve{U}}{\partial\breve{m}_1}\right)_{T,p}+p\left(\frac{\partial\breve{V}}{\partial\breve{m}_1}\right)_{T,p}\right)\right]\left(\frac{\partial\breve{V}}{\partial T}\right)_{p,\breve{m}_1} -\breve{c}_p\left[\breve{V}-\breve{m}_1\left(\frac{\partial\breve{V}}{\partial\breve{m}_1}\right)_{T,p}\right]\right\}$
m_2	$(m_1+m_2)\left\{\left[(\breve{U}+p\breve{V})+\breve{m}_2\left(\left(\frac{\partial\breve{U}}{\partial\breve{m}_1}\right)_{T,p}+p\left(\frac{\partial\breve{V}}{\partial\breve{m}_1}\right)_{T,p}\right)\right]\left(\frac{\partial\breve{V}}{\partial T}\right)_{p,\breve{m}_1} -\breve{c}_p\left[\breve{V}+\breve{m}_2\left(\frac{\partial\breve{V}}{\partial\breve{m}_1}\right)_{T,p}\right]\right\}$
S	$(m_1+m_2)\left\{\frac{\breve{c}_p}{T}\left[(\breve{U}-T\breve{S})\left(\frac{\partial\breve{V}}{\partial\breve{m}_1}\right)_{T,p}-\breve{V}\left(\left(\frac{\partial\breve{U}}{\partial\breve{m}_1}\right)_{T,p}-T\left(\frac{\partial\breve{S}}{\partial\breve{m}_1}\right)_{T,p}\right)\right] -\left(\frac{\partial\breve{V}}{\partial T}\right)_{p,\breve{m}_1}\left[(\breve{U}+p\breve{V})\left(\frac{\partial\breve{S}}{\partial\breve{m}_1}\right)_{T,p}-\breve{S}\left(\left(\frac{\partial\breve{U}}{\partial\breve{m}_1}\right)_{T,p}+p\left(\frac{\partial\breve{V}}{\partial\breve{m}_1}\right)_{T,p}\right)\right]\right\}$

Table IV-24
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

w', w \ x, y, z	p, V, S
T	$\breve{S}\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - \breve{V}\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}$
m_1	$(m_1 + m_2)\left\{\frac{\breve{C}_p}{T}\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right] - \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\right\}$
m_2	$-(m_1 + m_2)\left\{\frac{\breve{C}_p}{T}\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right] - \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\right\}$
U	$-(m_1 + m_2)\left\{\frac{\breve{C}_p}{T}\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - \breve{V}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right] - \left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p} - \breve{S}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\right\}$

Table IV-25
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

x, y, z / w', w	p, U, S
T	$\breve{S}\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} - \breve{U}\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}$
m_1	$(m_1 + m_2)\left\{\frac{\breve{C}_p}{T}\left[(\breve{U} - T\breve{S}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\right.$ $\left. + \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right] p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\right\}$
m_2	$(m_1 + m_2)\left\{\frac{\breve{C}_p}{T}\left[(\breve{U} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\right.$ $\left. + \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right] p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\right\}$
V	$(m_1 + m_2)\left\{\frac{\breve{C}_p}{T}\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - \breve{V}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\right.$ $\left. - \left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p} - \breve{S}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\right\}$

Table IV-26
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

x, y, z / w', w	[illegible]
T	$(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$
P	$-(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}$
U	$(m_1 + m_2)^2\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} + \breve{c}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right]$
S	$(m_1 + m_2)^2\left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right]$

Table IV-27
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}$$

w' \ x, y, z	m_1, m_2, U
T	$-(m_1 + m_2)\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} + p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right]$
p	$-(m_1 + m_2)\left[\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\right]$
V	$-(m_1 + m_2)^2\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} + \breve{c}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right]$
S	$-(m_1 + m_2)^2\left[p\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} + \frac{p\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right]$

Table IV-28
Jacobians of extensive functions for a
binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)} = \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

w' \ x, y, z	m_1, m_2, S
T	$-(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}$
p	$-(m_1 + m_2)\frac{\breve{C}_p}{T}$
V	$-(m_1 + m_2)^2\left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} + \frac{\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right]$
U	$(m_1 + m_2)^2\left[p\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} + \frac{p\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right]$

Table IV-29
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)} \cdot \frac{\partial(w, x, y, z)}{\partial(T, p, \breve{m}_1, m_2)}$$

x, y, z / w	m_1, V, U
T	$-(m_1+m_2)\left\{\left[(\breve U + p\breve V) - \breve m_1\left(\left(\frac{\partial \breve U}{\partial \breve m_1}\right)_{T,p} + p\left(\frac{\partial \breve V}{\partial \breve m_1}\right)_{T,p}\right)\right]\left(\frac{\partial \breve V}{\partial p}\right)_{T,\breve m_1} + \left[\breve V - \breve m_1\left(\frac{\partial \breve V}{\partial \breve m_1}\right)_{T,p}\right]T\left(\frac{\partial \breve V}{\partial T}\right)_{p,\breve m_1}\right\}$
P	$(m_1+m_2)\left\{\left[(\breve U + p\breve V) - \breve m_1\left(\left(\frac{\partial \breve U}{\partial \breve m_1}\right)_{T,p} + p\left(\frac{\partial \breve V}{\partial \breve m_1}\right)\right)\right]$ [illegible] $- \breve c_p\left[\breve V - \breve m_1\left(\frac{\partial \breve V}{\partial \breve m_1}\right)_{T,p}\right]\right\}$
m_2	$(m_1+m_2)^2\left[T\left(\frac{\partial \breve V}{\partial T}\right)^2_{p,\breve m_1} + \breve c_p\left(\frac{\partial \breve V}{\partial p}\right)_{T,\breve m_1}\right]$
S	[illegible]

Table IV-30
Jacobians of extensive functions for a
binary system of one phase

$$\frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, \breve{m}_1, m_2)}$$

z	m_1, V, S
T	$-(m_1 + m_2)\left\{\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1} + \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right\}$
p	$-(m_1 + m_2)\left\{\frac{\breve{C}_p}{T}\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right] - \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\right\}$
[illegible]	$(m_1 + m_2)^2\left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} + \frac{\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right]$
U	$(m_1 + m_2)^2\left\{\left[(\breve{U} + p\breve{V} - T\breve{S}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right] \times \left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} + \frac{\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right]\right\}$

Table IV-31
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)} : \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

w', w \ x, y, z	m_1, U, S
T	$-(m_1+m_2)\left\{\left[(\breve U - T\breve S) - \breve m_1\left(\left(\frac{\partial \breve U}{\partial \breve m_1}\right)_{T,p} - T\left(\frac{\partial \breve S}{\partial \breve m_1}\right)_{T,p}\right)\right]\left(\frac{\partial \breve V}{\partial T}\right)_{p,\breve m_1} - \left[\breve S - \breve m_1\left(\frac{\partial \breve S}{\partial \breve m_1}\right)_{T,p}\right]p\left(\frac{\partial \breve V}{\partial T}\right)_{p,\breve m_1}\right\}$
p	$-(m_1+m_2)\left\{\frac{\breve C_p}{T}\left[(\breve U - T\breve S) - \breve m_1\left(\left(\frac{\partial \breve U}{\partial \breve m_1}\right)_{T,p} - T\left(\frac{\partial \breve S}{\partial \breve m_1}\right)_{T,p}\right)\right] + \left[\breve S - \breve m_1\left(\frac{\partial \breve S}{\partial \breve m_1}\right)_{T,p}\right]p\left(\frac{\partial \breve V}{\partial T}\right)_{p,\breve m_1}\right\}$
m_2	$-(m_1+m_2)^2\left[p\left(\frac{\partial \breve V}{\partial T}\right)^2_{p,\breve m_1} + \frac{\breve C_p}{T}\left(\frac{\partial \breve V}{\partial p}\right)_{T,\breve m_1}\right]$
V	$-(m_1+m_2)^2\left\{\left[(\breve U + p\breve V - T\breve S) - \breve m_1\left(\left(\frac{\partial \breve U}{\partial \breve m_1}\right)_{T,p} + p\left(\frac{\partial \breve V}{\partial \breve m_1}\right)_{T,p} - T\left(\frac{\partial \breve S}{\partial \breve m_1}\right)_{T,p}\right)\right]$ [illegible] $\right\}$

Table IV-32
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(V, x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(U, x, y, z)}{\partial(T, p, m_1, m_2)}$$

x, y, z / w', w	m_2, V, U
T	$(m_1 + m_2)\left\{\left[(\breve{U} + p\breve{V}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1} + \left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right]T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\right\}$
p	[illegible]
m_1	$-(m_1 + m_2)^2\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} + \breve{c}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right]$
S	$(m_1 + m_2)^2\left\{\left[(\breve{U} + p\breve{V} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\right.$ [illegible]

Table IV-33
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

$w \backslash x, y, z$	m_2, V, S
T	$(m_1 + m_2)\left\{\left[\breve{V} + \breve{m}_2\left(\frac{\partial\breve{V}}{\partial\breve{m}_1}\right)_{T,p}\right]\left(\frac{\partial\breve{V}}{\partial T}\right)_{p,\breve{m}_1} + \left[\breve{S} + \breve{m}_2\left(\frac{\partial\breve{S}}{\partial\breve{m}_1}\right)_{T,p}\right]\left(\frac{\partial\breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right\}$
p	$(m_1 + m_2)\left\{\frac{\breve{C}_p}{T}\left[\breve{V} + \breve{m}_2\left(\frac{\partial\breve{V}}{\partial\breve{m}_1}\right)_{T,p}\right] - [\text{[illegible]}]_{T,p}\right]\left(\frac{\partial\breve{V}}{\partial T}\right)_{p,\breve{m}_1}\right\}$
n	$-(m_1 + \text{[illegible]})\left(\frac{\partial\breve{V}}{\partial p}\right)_{T,\breve{m}_1}$
a	$-(m_1 + m_2)^2\left\{\left[(\breve{U} + p\breve{V} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial\breve{U}}{\partial\breve{m}_1}\right)_{T,p} + p\left(\frac{\partial\breve{V}}{\partial\breve{m}_1}\right)_{T,p} - T\left(\frac{\partial\breve{S}}{\partial\breve{m}_1}\right)_{T,p}\right)\right]\left[\left(\frac{\partial\breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} + \frac{\breve{C}_p}{T}\left(\frac{\partial\breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right]\right\}$

Table IV-34
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(W, x, y, z)}{\partial(T, p, m_1, m_2)} = \frac{\partial(W, x, y, z)}{\partial(T, p, \breve{m}_1, \breve{m}_2)}$$

x, y, z / W	m_2, U, S
T	$(m_1 + m_2)\left\{\left[(\breve{U} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1} - \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right\}$
p	$(m_1 + m_2)\left\{\frac{\breve{c}_p}{[illegible]}\left[[illegible] + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{[illegible]}\right)_{T,p} [illegible] \left(\frac{\partial \breve{S}}{[illegible]}\right)_{T,p}\right)\right] + \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]p\left(\frac{\partial \breve{V}}{\partial T}\right)_{T,\breve{m}_1}\right\}$
m_1	[illegible]
V	$(m_1 + m_2)^2\left\{\left[(\breve{U} + p\breve{V} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right] \cdot \left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right]\right\}$

Table IV-35
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(V, x, y, z)}{\partial(T, p, m_1, m_2)}$$

x, y, z / w'	V, U, S
T	$-(m_1 + m_2)\left\{\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} - \breve{V}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right)\right] + \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p} - \breve{S}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right)\right]\right\}$
P	$-(m_1 + m_2)\left\{\frac{\breve{c}_p}{T}\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} - \breve{V}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right)\right] - \left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p} - \breve{S}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right)\right]\right\}$
. .	$(m_1 + m_2)^2\left\{\left[(\breve{U} + p\breve{V} - T\breve{S}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right)\right] \cdot \left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right]\right\}$
m_2	$-(m_1 + m_2)^2\left\{\left[(\breve{U} + p\breve{V} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right)\right] \left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right]\right\}$

In order to obtain the first partial derivative of any one of the seven quantities, T, p, m_1, m_2, V, U, S, with respect to any second quantity of the seven when any third, fourth, and fifth quantities of the seven are held constant, one has only to divide the value of the Jacobian in which the first letter in the first line is the quantity being differentiated and in which the second, third, and fourth letters in the first line are the quantities held constant by the value of the Jacobian in which the first letter of the first line is the quantity with respect to which the differentiation is taking place and in which the second, third, and fourth letters in the first line are the quantities held constant.

To obtain the relation among any seven derivatives having expressed them in terms of the same six derivatives,

$$\left(\frac{\partial V}{\partial T}\right)_{p,m_1}, \quad \left(\frac{\partial V}{\partial p}\right)_{T,m_1}, \quad \left(\frac{\partial V}{\partial m_1}\right)_{T,p}, \quad C_p, \quad \left(\frac{\partial U}{\partial m_1}\right)_{T,p}, \quad \left(\frac{\partial S}{\partial m_1}\right)_{T,p},$$

one can then eliminate the six derivatives from the seven equations, leaving a single equation connecting the seven derivatives. In addition to the relations among seven derivatives there are also degenerate cases in which there are relations among fewer than seven derivatives.

In case a relation is needed that involves one or more of the thermodynamic potential functions $H = U + pV$, $A = U - TS$, $G = U + pV - TS$, partial derivatives involving one or more of these functions can also be calculated as the quotients of two Jacobians, which can themselves be calculated by the same method used to calculate the Jacobians in Tables IV-1 to IV-35.

It will be noted that the expressions for the Jacobians in Tables IV-1 to IV-35 are not symmetrical with respect to the two mass fractions $\breve{m}_1$ and $\breve{m}_2$. If the Jacobians in these Tables had been expressed in terms of the derivatives $\frac{\partial \breve{V}}{\partial \breve{m}_1}$, $\frac{\partial \breve{V}}{\partial \breve{m}_2}$, $\frac{\partial \breve{U}}{\partial \breve{m}_1}$, $\frac{\partial \breve{U}}{\partial \breve{m}_2}$, $\frac{\partial \breve{S}}{\partial \breve{m}_1}$, and $\frac{\partial \breve{S}}{\partial \breve{m}_2}$, with respect to the two mass fractions, $\breve{m}_1$ and $\breve{m}_2$, rather than in terms of the derivatives, $\frac{\partial \breve{V}}{\partial \breve{m}_1}$, $\frac{\partial \breve{U}}{\partial \breve{m}_1}$, and $\frac{\partial \breve{S}}{\partial \breve{m}_1}$, with respect to the single mass fraction, $\breve{m}_1$, the symmetry of the expressions for the Jacobians with respect to $\breve{m}_1$ and $\breve{m}_2$ would have been preserved, but the Jacobians would not have been expressed in terms of the minimum number of first derivatives. In this case it would not have been possible to use the expressions for the Jacobians directly to obtain a desired relation among any seven first derivatives of the quantities, T, p, $\breve{m}_1$, $\breve{m}_2$, $\breve{V}$, $\breve{U}$, and $\breve{S}$, by elimination of the first derivatives, $\frac{\partial \breve{V}}{\partial T}$, $\frac{\partial \breve{V}}{\partial p}$, $\frac{\partial \breve{V}}{\partial \breve{m}_1}$, $\frac{\partial \breve{V}}{\partial \breve{m}_2}$, c_p, $\frac{\partial \breve{U}}{\partial \breve{m}_1}$, $\frac{\partial \breve{U}}{\partial \breve{m}_2}$, $\frac{\partial \breve{S}}{\partial \breve{m}_1}$, and $\frac{\partial \breve{S}}{\partial \breve{m}_2}$, from the seven equations for the seven first derivatives. Actually with the use of the Jacobians in Tables IV-1 to IV-35 which are expressed in terms of the minimum number of fundamental derivatives, $\frac{\partial \breve{V}}{\partial T}$, $\frac{\partial \breve{V}}{\partial p}$, $\frac{\partial \breve{V}}{\partial \breve{m}_1}$, c_p, $\frac{\partial \breve{U}}{\partial \breve{m}_1}$, and $\frac{\partial \breve{S}}{\partial \breve{m}_1}$, in spite of the fact that these expressions are unsymmetrical with respect to $\breve{m}_1$ and $\breve{m}_2$, it does not make any difference in the final result which component is chosen as component 1 and which component is chosen as component 2. For example, if one thinks of a solution of water and ethyl alcohol and if water is chosen as component 1, then from Table IV-32 one obtains the derivative $\left(\frac{\partial S}{\partial m_1}\right)_{m_2, V, U}$ equal to

$$-\frac{1}{T}\left[(\breve{U} + p\breve{V} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p}\right)\right].$$

Now from Table IV-29 one obtains the derivative $\left(\frac{\partial S}{\partial m_2}\right)_{m_1, V, U}$

equal to

$$-\frac{1}{T}\left[(\breve{U} + p\breve{V} - T\breve{S}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p}\right)\right].$$

On account of the fact that $\breve{m}_1 + \breve{m}_2 = 1$, one has $\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} = -\left(\frac{\partial \breve{U}}{\partial \breve{m}_2}\right)_{T,\,p}$. Thus $\left(\frac{\partial S}{\partial m_2}\right)_{m_1,\,V,\,U}$ is also equal to

$$-\frac{1}{T}\left[(\breve{U} + p\breve{V} - T\breve{S}) + \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_2}\right)_{T,\,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_2}\right)_{T,\,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p}\right)\right].$$

Consequently the same value would be obtained for the partial derivative of the total entropy with respect to the mass of water regardless of whether water were chosen as component 1 or as component 2.

Appendix A to Part IV

Equations for energy and entropy in the case of a binary system of one phase and of variable total mass developed on the basis of an expression for heat in the case of an open system

In the author's Carnegie Institution of Washington Publication No, 408A[1] equations were developed for energy and entropy in the case of open systems on the basis of an expression for the heat received by an open system. In the case of a binary system of one phase undergoing reversible changes of temperature, pressure, mass of component 1, and mass of component 2, the heat received was shown to be represented by the integral in the following equation

$$Q = \int_{T_0,\,p_0,\,m_{1_0},\,m_{2_0}}^{T,\,p,\,m_1,\,m_2} \left\{ \left(\frac{dQ}{dT}\right)_{p,\,m_1,\,m_2} dT + \left(\frac{dQ}{dp}\right)_{T,\,m_1,\,m_2} dp + \left(\frac{dQ}{dm_1}\right)_{T,\,p,\,m_2} dm_1 + \left(\frac{dQ}{dm_2}\right)_{T,\,p,\,m_1} dm_2 \right\}$$

$$= \int_{T_0,\,p_0,\,m_{1_0},\,m_{2_0}}^{T,\,p,\,m_1,\,m_2} \left\{ (m_1 + m_2)\, c_p\, dT + (m_1 + m_2)\, l_p\, dp + l_{m_1} dm_1 + l_{m_2} dm_2 \right\}, \qquad \text{(IV-A-1)}$$

where l_{m_1} denotes the reversible heat of addition of component 1 at constant temperature, constant pressure, and constant mass of component 2, and l_{m_2} denotes the reversible

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[1] Tunell, G., *Thermodynamic Relations in Open Systems,* Carnegie Institution of Washington Publication No. 408A, 1977.

heat of addition of component 2 at constant temperature, constant pressure, and constant mass of component 1.[2] In the case of a binary system of one phase undergoing reversible changes of temperature, pressure, mass of component 1, and mass of component 2, the energy change was shown to be represented by the integral in the following equation

$$U(T, p, m_1, m_2) - U(T_0, p_0, m_{1_0}, m_{2_0})$$

$$= \int_{T_0, p_0, m_{1_0}, m_{2_0}}^{T, p, m_1, m_2} \left\{ (m_1 + m_2)\left[\breve{c}_p - p\frac{\partial \breve{V}}{\partial T}\right] dT + (m_1 + m_2)\left[\breve{l}_p - p\frac{\partial \breve{V}}{\partial p}\right] dp \right.$$

$$+ \left[l_{m_1} - p\breve{m}_2\frac{\partial \breve{V}}{\partial \breve{m}_1} - p\breve{V} + \breve{H}' \right] dm_1$$

$$\left. + \left[l_{m_2} + p\breve{m}_1\frac{\partial \breve{V}}{\partial \breve{m}_1} - p\breve{V} + \breve{H}'' \right] dm_2 \right\}, \qquad \text{(IV-A-2)}$$

where $\breve{m}_1$ denotes the mass fraction of component 1, $\breve{m}_2$ denotes the mass fraction of component 2, $\breve{H}'$ denotes the specific enthalpy of pure component 1 in equilibrium with the binary solution across a semipermeable membrane permeable only to component 1, and $\breve{H}''$ denotes the specific enthalpy of pure component 2 in equilibrium with the binary solution across a semipermeable membrane permeable only to component 2.[3] In the

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[2] Tunell, G., Carnegie Institution of Washington Publication No. 408A, 1977, p. 40, equation (B-6), p. 42, equations (B-10), and (B-11), p, 46, equation (B-19), and P. 47, equation (B-20).

[3] Tunell, G., Carnegie Institution of Washington Publication No. 408A, 1977, p. 52, equation (B-35).

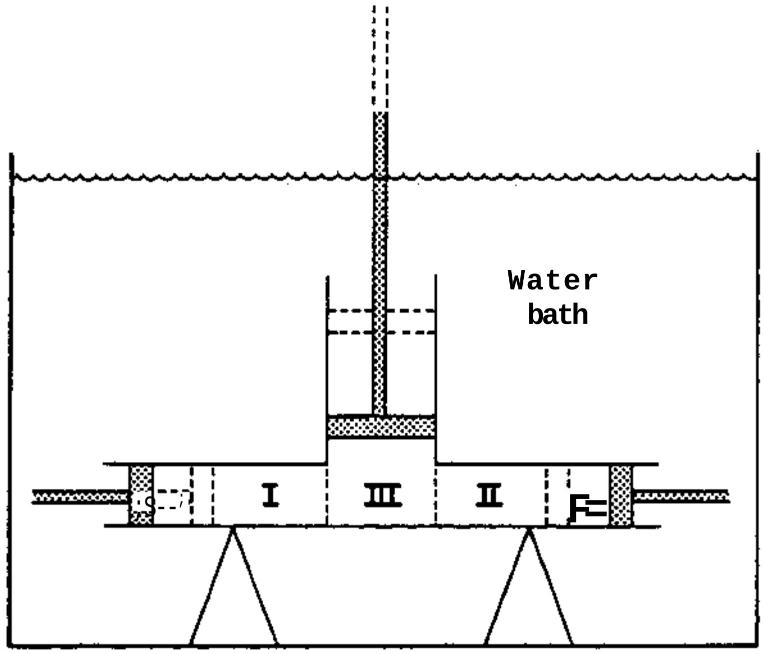

Figure IV-A-1

same case the entropy change was shown to be represented by the integral in the following equation

$$S(T, p, m_1, m_2) - S(T_0, p_0, m_{1_0}, m_{2_0})$$

$$= \int_{T_0, p_0, m_{1_0}, m_{2_0}}^{T, p, m_1, m_2} \left\{ (m_1 + m_2) \frac{\breve{c}_p}{T} dT + (m_1 + m_2) \frac{\breve{l}_p}{T} dp + \left[\frac{l_{m_1}}{T} + \breve{S}' \right] dm_1 + \left[\frac{l_{m_2}}{T} + \breve{S}'' \right] dm_2 \right\} ,$$

(IV-A-3)

where $\breve{S}'$ denotes the specific entropy of pure component 1 in equilibrium with the binary solution across a semipermeable membrane permeable only to component 1, and $\breve{S}''$ denotes the specific entropy of pure component 2 in equilibrium with the binary solution across a semipermeable membrane permeable only to component 2.[4,5] The derivation of these equations for heat, energy, and entropy was based on a detailed operational analysis of a system of three chambers immersed in a water bath the temperature of which could be controlled (Figure IV-A-1). Chambers I and II containing pure components 1 and 2 were separated by semipermeable membranes from chamber III, which contained a solution of components 1 and 2. The

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[4] **Tunell, G.,** Carnegie Institution of Washington **Publication** No. 408A, 1977, p. 56, equation (B-46).

[5] For an explanation of methods for obtaining experimental values for the l's see G. **Tunell,** Idem, pages 46 and 59-62.

membrane separating chambers I and III was supposed permeable only to component 1; similarly, the membrane separating chambers II and III was supposed permeable only to component 2. When the pressures exerted by the three pistons on the contents of the three chambers were changed with maintenance of osmotic equilibrium, causing movement of the three pistons, and when the temperature of the water bath was changed, causing a flow of heat to or from the materials in the three chambers, the change of energy of the materials in the three chambers, which together constituted a closed system, was given by the equation

$$U_2 - U_1 = Q - W, \qquad \text{(IV-A-4)}$$

where U_2 denotes the energy of the materials in the three chambers in the final state, U_1 denotes the energy of the materials in the three chambers in the initial state, Q denotes the heat received by the materials in the three chambers from the water bath (a positive or negative quantity), and W denotes the work done on the three pistons by the materials in the three chambers (a positive or negative quantity). Note that maintenance of osmotic equilibrium required that of the three pressures in the three chambers only one was independent, the other two were functions of the temperature, the concentration in chamber III, and the one pressure taken as independent. The materials in the three chambers I, II, and III, together constituted a closed system undergoing a reversible change of state. Consequently we have

$$S_2 - S_1 = \int_1^2 \frac{dQ}{T}, \qquad \text{(IV-A-5)}$$

where S_f denotes the entropy of the materials in the three chambers in the final state and S_i denotes the entropy of the materials in the three chambers in the initial state. Thus the total change in energy and the total change in entropy of the closed system consisting of the materials in the three chambers were experimentally determinable. Finally, by subtraction of the energy changes of the pure components 1 and 2 in the side chambers I and II from the total energy change of the materials in the three chambers, the change in energy of the binary solution in chamber III as represented in equation (IV-A-2) was derived. Likewise by subtraction of the entropy changes of the pure components 1 and 2 in the side chambers I and II from the total entropy change of the materials in the three chambers, the change in entropy of the binary solution in chamber III as represented in equation (IV-A-3) was derived. For the details of these proofs the reader is referred to Appendix B of the author's Carnegie Institution of Washington Publication No. 408A.[6] It is to be noted that the only physical information used in the derivations of equations (IV-A-1), (IV-A-2), and (IV-A-3) in addition to the well established thermodynamic relations for closed systems, was the fact that when mass of constant composition is added reversibly to an open system of the same composition at constant temperature and constant pressure no heat is added.[7]

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[6] Tunell, G., Carnegie Institution of Washington Publication No. 408A, 1977, pp. 34-58.

[7] Cf. L.J. Gillespie and J.R. Coe, Jr., Jour. Phys. Chem., Vol. 1, p. 105, 1933, and G. Tunell, Carnegie Institution of Washington Publication No. 408A, 1977, pp. 18-24.

It was not necessary to make use of any definition of work in the case of an open system when masses are being transferred to or from the system in the derivation of equations (IV-A-1), (IV-A-2), and (IV-A-3). However, according to the definition of work done by an open system used by Goranson[8] and by Van Wylen[9] we have

$$dW = pdV . \qquad \text{(IV-A-6)}$$

In Appendix A to Part II of this text reasons for the acceptance of this definition of work in the case of an open system when masses are being transferred to or from the system were set forth in detail.

The correct differential equation for the energy change in an open system, when use is made of definitions of heat received and work done in the case of open systems, was given by Hall and Ibele in their treatise entitled *Engineering Thermodynamics.* They[10] stated that "A general equation for energy change in an open system can be written

$$dE = dQ - dW + \underset{i}{l}(e + pv)_i dm_i . \qquad (7.25)"$$

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[8] Goranson, R.W., Carnegie Institution of Washington Publication No. 408, 1930, pp. 39, 44.

[9] Van Wylen, G.J., *Thermodynamics,* John Wiley and Sons Inc., New York, 1959, pp. 49, 75-77, 80•

[10] Hall, N.A., and W.E., Ibele, *Engineering Thermodynamics*, Prentice-Hall, Inc., Englewood Cliffs, N.J., 1960, p. 108.

In this equation *dE* denotes the energy change of the open system, *dQ* the heat received by the open system, *dW* the work done by the open system, e the specific energy of pure component i in equilibrium with the open system across a semipermeable membrane permeable only to component i, p the pressure of pure component i in equilibrium with the open system across a membrane permeable only to component i, and *v* the specific volume of pure component i in equilibrium with the open system across a semipermeable membrane permeable only to component *i*. This equation is consistent with equation (IV-A-2) of this text as well as with the equation of Gillespie and Coe and with the Gibbs differential equation, as we proceed to show. According to Gillespie and Coe[11]

$$dS = \frac{dQ}{T} + \sum_i \breve{S}_i dm_i \ ,$$

where *dS* denotes the increase in entropy of an open system, *dQ* the heat received by the open system, $\breve{S}_j$ the specific entropy of pure component i in equilibrium with the open system across a semipermeable membrane permeable only to component i, and dw_j the mass of component i added to the open system. Thus we have

$$dQ = TdS - \sum_i T\breve{S}_i dm_i \ .$$

Substituting this value of *dQ* in the equation of Hall and

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[11] Gillespie, L.J., and J.R.. Coe, Jr., Jour. Chenu Phys., 1, 105, 1933.

Ibele we have

$$dU = TdS - dW + \sum_i (\breve{U}_i + p\breve{V}_i - T\breve{S}_i)\,dm_i \, .$$

According to Goranson,[12] Van Wylen,[13] and Professor Wild[14]

$$dW = pdV$$

in the case of an open system. Thus we obtain

$$dU = TdS - pdV + \sum_i \breve{G}_i\,dm_i \, ,$$

where $\breve{G}_i$ denotes the specific Gibbs function of pure component i in equilibrium with the solution across a semipermeable membrane permeable only to component i. Since Gibbs proved that at equilibrium the chemical potentials of a component on both sides of a semipermeable membrane are equal and since the chemical potential u of a pure component is equal to the specific Gibbs function of this component, we thus arrive at the result

$$dU = TdS - pdV + \sum_i \mu_i\,dm_i \, ,$$

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[12] Goranson, RJi., Carnegie Institution of Washington Publication No, 408, 1930, pp. 39 and 44.

[13] Van Wylen, op. cit, pp. 49, 75-77, 80.

[14] Private communication from Professor R.L. Wild, who was formerly the Chairman of the Physics Department of the University of California at Riverside.

where y^ denotes the chemical potential of component *i* in the open system (solution) and *dm*± denotes the mass of component i added to the open system. We have thus demonstrated that the equation of Gillespie and Coe and the equation of Hall and Ibele are consistent with the Gibbs differential equation.

Transformation of the work and heat line integrals from one coordinate space to other coordinate spaces in the case of a binary system of one phase and of variable total mass

As in the case of a one component system of one phase and of variable mass it is also true in the case of a binary system of one phase and of variable total mass that it is not necessary to define either work or heat when masses are being transferred to or from the system in order to obtain the energy and the entropy as functions of the absolute thermodynamic temperature, the pressure, and the masses of the two components from experimental measurements. Thus the derivation of the Jacobians listed in Tables IV-1 to IV-35 did not depend upon definitions of work done or heat received in the case of a binary system of one phase and of variable total mass when masses are being transferred to or from the system.

For some purposes, however, it is useful to have definitions of work and heat in the case of a binary system of one phase and of variable total mass. If the conclusion of Van Wylen and Professor Wild be accepted that it cannot be said that work is done at a stationary boundary across which mass is transported, then the work W done by a binary system of one phase and of variable total mass can be represented by the line integral

$$W = \int_{T_0,\, p_0,\, m_{1_0},\, m_{2_0}}^{T_f,\, p_f,\, fill\$\, 21?2} \left\{ p\, f\, dT + p \wedge dp + p f_{idmi} + p f £<* \, m_2 \right\} \qquad \text{(IV-B-1)}$$

in (T, p, m_1, m_2)-space. Furthermore it was shown in Appendix IV-A that the heat Q received by such a system is represented by the line integral

$$\int_{T_0, p_0, m_{1_0}, m_{2_0}}^{T, p, m_1, m_2} \ldots + m_2) \breve{l}_p dp + l_{m_1} dm_1 + l_{m_2} dm_2 \Big\} \qquad \text{(IV-B-2)}$$

in (T, p, m_1, m_2)-space, where l_{m_1} denotes the reversible heat of addition of component 1 at constant temperature, constant pressure and constant mass of component 2, and l_{m_2} denotes the reversible heat of addition of component 2 at constant temperature, constant pressure, and constant mass of component 1. In order to obtain the total derivative of the work done along a straight line parallel to one of the coordinate axes in any other coordinate space one obtains from Tables IV-1 to IV-35 the partial derivative of the volume with respect to the quantity plotted along that axis when the quantities plotted along the other axes are held constant and one multiplies this partial derivative by the pressure. The total derivative of the heat received along a straight line parallel to one of the coordinate axes in any other space, on the other hand, cannot be obtained by multiplication of the partial derivative of the entropy by the absolute thermodynamic temperature when reversible transfers of masses to or from the system are involved. In such cases the total derivatives of the heat received along lines parallel to coordinate axes in any desired coordinate space can be derived in terms of the total derivatives of the heat received along lines parallel to the coordinate axes in (T, p, m_1, m_2)-space by transformation of the heat line integrals by an extension of the method set forth in Appendix C to Part II. Following is an example of such a transformation. In the case of a binary system of one phase and of variable total mass the heat line integral extended along a path in (T, m_1, m_2, V)-space is

$$Q = \int_{T_0, m_{1_0}, m_{2_0}, V_0}^{T, m_1, m_2, V} \left\{ \left(\frac{dQ}{dT}\right)_{m_1, m_2, V} dT + \left(\frac{dQ}{dm_1}\right)_{T, m_2, V} dm_1 + \left(\frac{dQ}{dm_2}\right)_{T, m_1, V} dm_2 + \left(\frac{dQ}{dV}\right)_{T, m_1, m_2} dV \right\}$$

$$= \int_{T_0, m_{1_0}, m_{2_0}, V_0}^{T, m_1, m_2, V} \left\{ (m_1 + m_2)\breve{c}_V dT + \left(\frac{dQ}{dm_1}\right)_{T, m_2, V} dm_1 + \left(\frac{dQ}{dm_2}\right)_{T, m_1, V} dm_2 + l_V dV \right\} . \qquad \text{(IV-B-3)}$$

The derivatives $\left(\frac{dQ}{dT}\right)_{m_1, m_2, V}$, $\left(\frac{dQ}{dm_1}\right)_{T, m_2, V}$, $\left(\frac{dQ}{dm_2}\right)_{T, m_1, V}$, and $\left(\frac{dQ}{dV}\right)_{T, m_1, m_2}$ can then be evaluated as quotients of two determinants. Thus we have

$$\left(\frac{\partial Q}{\partial T}\right)_{m_1, m_2, V} = (m_1 + m_2)\breve{c}_v = \frac{\begin{vmatrix} \frac{\partial Q}{\partial T} & \frac{\partial Q}{\partial p} & \frac{\partial Q}{\partial m_1} & \frac{\partial Q}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}}{\begin{vmatrix} \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}}$$

$$= \left\{ \frac{\partial Q}{\partial T}\left[\frac{\partial V}{\partial p}\right] - \frac{\partial Q}{\partial p}\left[\frac{\partial V}{\partial T}\right] + \frac{\partial Q}{\partial m_1}\left[0\right] - \frac{\partial Q}{\partial m_2}\left[0\right] \right\}$$

$$\div \left\{ 1 \cdot \left[\frac{\partial V}{\partial p}\right] - 0 \cdot \left[\frac{\partial V}{\partial T}\right] + 0 \cdot \left[0\right] - 0 \cdot \left[0\right] \right\}$$

$$= \left\{ (m_1 + m_2)^2 \breve{c}_p \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1} - (m_1 + m_2)^2 \breve{l}_p \left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} \right\}$$

$$\div \left\{ (m_1 + m_2) \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1} \right\}$$

$$= \left\{ (m_1 + m_2) \left[\breve{c}_p \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1} + T \left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} \right] \right\} \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}, \tag{IV-B-4}$$

$$\left(\frac{\partial Q}{\partial m_1}\right)_{T,\,m_2,\,V} = \frac{\begin{vmatrix} \frac{\partial Q}{\partial T} & \frac{\partial Q}{\partial p} & \frac{\partial Q}{\partial m_1} & \frac{\partial Q}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}}{\begin{vmatrix} \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}}$$

$$= \left\{ \frac{\partial Q}{\partial T}\left[\,[illegible]\,\right] - \frac{\partial Q}{\partial p}\left[\,[illegible]\ \partial m_1\,\right] + \frac{\partial Q}{\partial m_1}\left[\,[illegible]\ \partial p\,\right] - \frac{\partial Q}{\partial m_2}\left[0\right] \right\}$$

$$\div \left\{ 0\left[0\right] - 0\left[-\frac{\partial V}{\partial m_1}\right] + \frac{\partial m_1}{\partial m_1}\left[-\frac{\partial V}{\partial p}\right] - 0\left[0\right] \right\}$$

$$= \left\{ (m_1 + m_2)\breve{l}_p\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}\right] - l_{m_1}(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1} \right\}$$

$$\div \left\{ -(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1} \right\}$$

$$= \left\{ T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}\right] + l_{m_1}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1} \right\} \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}, \tag{IV-B-5}$$

$$
\left(\frac{\partial Q}{\partial m_2}\right)_{T,m_1,V} = \frac{\begin{vmatrix} \frac{\partial Q}{\partial T} & \frac{\partial Q}{\partial p} & \frac{\partial Q}{\partial m_1} & \frac{\partial Q}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}}{\begin{vmatrix} \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}}
$$

$$
= \left\{\frac{\partial Q}{\partial T}[0] - \frac{\partial Q}{\partial p}\left[\frac{\partial V}{\partial m_2}\right] + \frac{\partial Q}{\partial m_1}[0] - \frac{\partial Q}{\partial m_2}\left[-\frac{\partial V}{\partial p}\right]\right\}
$$

$$
\div \left\{0 \cdot [0] - 0 \cdot \left[\frac{\partial V}{\partial m_2}\right] + 0 \cdot [0] - \frac{\partial m_2}{\partial m_2}\left[-\frac{\partial V}{\partial p}\right]\right\}
$$

$$
= \left\{-(m_1 + m_2)\breve{l}_p\left(\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right) + l_{m_2}(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right\}
$$

$$
\div \left\{(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right\}
$$

$$
= \left\{T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right] + l_{m_2}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right\} \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}, \tag{IV-B-6}
$$

$$\left(\frac{\partial Q}{\partial V}\right)_{T,\, m_1,\, m_2} = l_V = \frac{\begin{vmatrix} \frac{\partial Q}{\partial T} & \frac{\partial Q}{\partial p} & \frac{\partial Q}{\partial m_1} & \frac{\partial Q}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \end{vmatrix}}{\begin{vmatrix} \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \end{vmatrix}}$$

$$= \left\{ \frac{\partial Q}{\partial T}\begin{bmatrix}0\end{bmatrix} - \frac{\partial Q}{\partial p}\begin{bmatrix}1\end{bmatrix} + \frac{\partial Q}{\partial m_1}\begin{bmatrix}0\end{bmatrix} - \frac{\partial Q}{\partial m_2}\begin{bmatrix}0\end{bmatrix}\right\}$$

$$\div \left\{ \frac{\partial V}{\partial T}\begin{bmatrix}0\end{bmatrix} - \frac{\partial V}{\partial p}\begin{bmatrix}1\end{bmatrix} + \frac{\partial V}{\partial m_1}\begin{bmatrix}0\end{bmatrix} - \frac{\partial V}{\partial m_2}\begin{bmatrix}0\end{bmatrix}\right\}$$

$$= \left\{ (m_1 + m_2)\breve{l}_p \right\} \div \left\{ (m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1} \right\}$$

$$= \left\{ -T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1} \right\} \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1} .$$

(IV-B-7)

The corresponding values of the partial derivatives of the entropy obtained from Tables IV-26, IV-10, IV-7, and IV-6 are as follows:

$$\left(\frac{\partial S}{\partial T}\right)_{m_1, m_2, V} = \left\{(m_1 + m_2)\left[\frac{\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1} + \left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1}\right]\right\} \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1} .$$

(IV-B-8)

$$\left(\frac{\partial S}{\partial m_1}\right)_{T, m_2, V} = \left\{\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\right.$$

$$\left. + \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right\} \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$$

$$= \left\{\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\right.$$

$$\left. + \left[\left(\frac{\partial S}{\partial m_1}\right)_{T, p, m_2}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right\} \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$$

$$= \left\{\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\right.$$

$$\left. + \left[\frac{l_{m_1}}{T} + \breve{S}'\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right\} \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1} ,$$

(IV-B-9)

$$\left(\frac{\partial S}{\partial m_2}\right)_{T,\,m_1,\,V} = \left\{\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}\right.$$

$$\left. + \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right\} \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}$$

$$= \left\{\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right) \text{[illegible]}\right.\right.$$

$$\left. + \left[\left(\frac{\partial S}{\partial m_2}\right)_{T,\,p,\,m_1}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right\} \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}$$

$$= \left\{\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}\right]\right.$$

$$\left. + \left[\frac{l_{m_2}}{T} + \breve{S}''\right]\left(\frac{\partial \breve{V}}{\text{[illegible]}}\right)_{\text{[illegible]},\,\breve{m}_1}\right\} \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1},$$

(IV-B-10)

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[1] From equations (IV-22) and (IV-23) we have

[illegible] ∂m_1 [illegible] $\partial \breve{m}_1$ [illegible] ∂m_2 [illegible] $\breve{m}_1\left(\frac{\partial}{\partial \breve{m}_1}\right)$ [illegible].

Also from equation (XV-A-3) we have $\left(\frac{\partial S}{\partial m_1}\right)_{T,\,p,\,m_2}$ = [illegible] + $\breve{S}'$

and $\left(\frac{\partial S}{\partial m_2}\right)_{T,\,p,\,m_1}$ = [illegible] + $\breve{S}''$, where $\breve{S}'$ denotes the specific entropy of pure component 1 in equilibrium with the binary solution across a semipermeable membrane permeable only to component 1, and $\breve{S}''$ the specific entropy of pure component 2 in equilibrium with the binary solution across a semipermeable membrane permeable only to component 2,

and

$$\left(as\right)_{T,\, m_1,\, m_2} \;\_\; \left[\, fiil \right)_{p,\, m_1} \; Lfll\Big)_{\partial p\, ,\, T,\, m_1} . \qquad \text{(iv-B-ii)}$$

Thus it follows from (IV-B-4), (IV-B-7), (IV-B-8), and (IV-B-11) that

$$\left(f\right)_{m_1,\, m_2,\, V} = T\left(\frac{\partial S}{\partial T}\right)_{m_1,\, m_2,\, V} \qquad \text{(IV-B-12)}$$

and

$$\left(\S\right) \; , \quad T\left(\S\right) \qquad \text{(IV-B-U)}$$

but, finally, it also follows from (IV-B-5), (IV-B-6) (IV-B-9), and (IV-B-10) that

$$\left(\frac{dQ}{dm_1}\right)_{T,\, m_2,\, V} \neq T\left(\frac{\partial S}{\partial m_1}\right)_{T,\, m_2,\, V} \qquad \text{(IV-B-14)}$$

and

$$\left(f\right)_{T,\, m_1,\, V} \neq jf!\wedge \Big)_{T,\, m_1,\, V} . \qquad \text{(IV-B-15)}$$

Appendix C to Part IV

Discussion of the tables of thermodynamic.formulas for multi-component systems presented in Carnegie Institution of Washington Publication No. 408 by R.W. Goranson

On account of the fact that Goranson accepted the erroneous assumption of Sir Joseph Larmor[1] that in the case of the Gibbs differential equation,

$$dU = TdS - pdV + \text{Uicfoi} + Vidm_2 \ \ldots + V_n dm_{n9}$$

TdS represents *dQ* and that *dQ* represents an infinitesimal amount of heat which is acquired in a specified state of the system at a temperature T_9 Goranson[f]s basic equations for the energy and the entropy of a multi-component system are incorrect. Goranson[T]s equation for the energy change of a binary system undergoing changes of temperature, pressure, and masses of the two components

$U(T,$ p, *Wif* 072) - *U(TQ, po* /771*$_0$, m_{2_0})

$T_9\, p_9\, mi > m_2$

II dT/ I I ** CiT/ I

= J {(mi + ra2) [^p " P g ^ F + (mi + ^2) [l_p - PjrUp

Tot Po, iZ?i$_{0>}$ i7I2$_Q$

(IV-C-1)

$$+ \left[l_{m_1} - p\breve{m}_2 \frac{\partial \breve{V}}{\partial \breve{m}_1} - p\breve{V} + Ui \right] dm_1 + \left[l_{m2} + \breve{p}m\wedge - p\breve{V} + M_2 \right] dm_2 \Big\},$$ [2]

---

[1] Larmor, Sir Joseph, Proc. Roy. Soc. London, 75, 289-290, 1905.

[2] Goranson, R.W., Carnegie Institution of Washington Publication No. 408, 1930, the first equation in §32 on page 48.

where l_{m_1} denotes the reversible heat of addition of component 1 at constant temperature, constant pressure, and constant mass of component 2, l_{m_2} denotes the reversible heat of addition of component 2 at constant temperature, constant pressure, and constant mass of component 1, $\breve{m}_1$ denotes the mass fraction $m_1/(m_1 + m_2)$, $\breve{m}_2$ denotes the mass fraction $m_2/(m_1 + m_2)$, μ_1 denotes the chemical potential of component 1, and μ_2 denotes the chemical potential of component 2, should be replaced by equation (IV-A-2) of this text which is repeated here as aquation (IV-C-2)

$$U(T, p, m_1, m_2) - U(T_0, p_0, m_{1_0}, m_{2_0})$$

$$= \int_{T_0, p_0, m_{1_0}, m_{2_0}}^{T, p, m_1, m_2} \Big\{ (m_1 + m_2)\Big[c_p - p\frac{\partial \breve{V}}{\partial T}\Big] dT + (m_1 + m_2)\Big[l_p - p\frac{\partial \breve{V}}{\partial p}\Big] dp$$

$$+ \Big[l_{m_1} - p\breve{m}_2\frac{\partial \breve{V}}{\partial \breve{m}_1} - p\breve{V} + \breve{H}'\Big] dm_1 + \Big[l_{m_2} + p\breve{m}_1\frac{\partial \breve{V}}{\partial \breve{m}_1} - p\breve{V} + \breve{H}''\Big] dm_2 \Big\} , \qquad \text{(IV-C-2)}$$

where $\breve{H}'$ and $\breve{H}''$ denote the specific enthalpies of the pure components 1 and 2 in equilibrium with the solution across semipermeable membranes permeable only to components 1 and 2, respectively. Similar corrections are to be applied in the incorrect equation for the energy U in the case of a multi-component system on page 60 of Carnegie Institution of Washington Publication No. 408 [equation (1) in §41].

Likewise Goranson's equation for the entropy change of a binary system undergoing reversible changes of temperature, pressure, and masses of the two components, the first equation in §52 [equation (2)] on page 52 of Carnegie Institution of Washington Publication No. 408

$$S(T, p, m_1, m_2) - S(T_0, p_0, m_{1_0}, m_{2_0})$$

$$= \int_{T_0,\, p_0,\, m_{1_0},\, m_{2_0}}^{T,\, p,\, m_1,\, m_2} \left\{ (m_1 + m_2)\frac{\breve{c}_p}{T}\, dT + (m_1 + m_2)\frac{\breve{l}_p}{T}\, dp \right.$$

$$\left. + \frac{l_{m_1}}{T}\, dm_1 + \frac{l_{m_2}}{T}\, dm_2 \right\} \qquad \text{(IV-C-3)}$$

should be replaced by equation (IV-A-3) of this text which is repeated here as equation (IV-C-4)

$$S(T, p, m_1, m_2) - S(T_0, p_0, m_{1_0}, m_{2_0})$$

$$= \int_{T_0,\, p_0,\, m_{1_0},\, m_{2_0}}^{T,\, p,\, m_1,\, m_2} \left\{ (m_1 + m_2)\frac{\breve{c}_p}{T}\, dT + (m_1 + m_2)\frac{\breve{l}_p}{T}\, dp \right.$$

$$\left. + \left[\frac{l_{m_1}}{T} + \breve{s}'\right] dm_1 + \left[\frac{l_{m_2}}{T} + \breve{s}''\right] dm_2 \right\}, \qquad \text{(IV-C-4)}$$

where S' denotes the specific entropy of pure component 1 in equilibrium with the binary solution across a semipermeable membrane permeable only to component 1, and S'' denotes the specific entropy of pure component 2 in equilibrium with the binary solution across a semipermeable membrane permeable only to component 2. Similar corrections are to be applied to the incorrect equation for the entropy S in the case of a multi-component system on page 64 of Carnegie Institution of Washington Publication No. 408 (first equation in §43).

In Goranson's Tables of Thermodynamic Relations for First Derivatives expressions are listed such that any first derivative of one of the quantities, absolute thermodynamic temperature, pressure, mass of a component, volume, energy, entropy, Gibbs function, enthalpy, Helmholtz function, work, or heat with respect to any second of these quantities, certain other quantities being held constant, should be obtainable in terms of the standard derivatives,

$$\left(\frac{\partial v}{\partial p}\right)_{T, m_1, \ldots, m_n}, \quad \left(\frac{\partial v}{\partial T}\right)_{p, m_1, \ldots, m_n}, \quad \left(\frac{\partial v}{\partial m_i}\right)_{T, p, m_i}, \quad \text{denoting}$$

all the component masses except m_i, $(m_1 + \ldots + m_n)c_{p}$, $i = 1, \ldots, n$, and μ_k, $k = 1, \ldots, n$, by division of one of the listed expressions by a second listed expression, the same quantities being held constant in each of these two listed expressions.

The expressions listed by Goranson for first derivatives in his Groups 1-8 are for the case in which all masses are held constant and are the same as the expressions listed by Bridgman for this case and the same as the Jacobians listed in Table 1-1 of this text. Unfortunately very many of the expressions listed by Goranson in his remaining Groups for first derivatives (Groups 9 - 162) are invalidated by his erroneous assumption that $dQ = TdS$ when there is reversible transfer of mass as well as heat. Thus for example in Goranson's Group 18 in which p, m_i, and S are held constant the following expressions are listed:

Group 18

(According to Goranson, Carnegie Institution of Washington Publication No. 408, p. 181)

p, m_i, S constant

$$(\partial T) = -\frac{l_{m_k}}{T}$$

$$(\partial m_k) = (m_1 + \ldots + m_n)\frac{\breve{c}_p}{T}$$

$$(\partial V) = -\frac{l_{m_k}}{T}\frac{\partial V}{\partial T} + \frac{\breve{c}_p(m_1 + \ldots + m_n)}{T}\frac{\partial V}{\partial m_k}$$

$$(\partial U) = \frac{p}{T}\, l_{m_k}\frac{\partial V}{\partial T} + (m_1 + \ldots + m_n)\frac{\breve{c}_p}{T}\left[\mu_k - p\frac{\partial V}{\partial m_k}\right]$$

$$(\partial G) = \frac{1}{T}\left[S l_{m_k} + (m_1 + \ldots + m_n)\breve{c}_p\mu_k\right]$$

$$(\partial H) = \frac{1}{T}(m_1 + \ldots + m_n)\breve{c}_p\mu_k$$

$$(\partial A) = \frac{1}{T}\left[l_{m_k}\left(S + p\frac{\partial V}{\partial T}\right) + (m_1 + \ldots + m_n)\breve{c}_p\left(\mu_k - p\frac{\partial V}{\partial m_k}\right)\right]$$

$$(dW) = p\frac{l_{m_k}}{T}\frac{\partial V}{\partial T} - \frac{\breve{c}_p(m_1 + \ldots + m_n)}{T}\, p\frac{\partial V}{\partial m_k}$$

$$(dQ) = 0$$

The corrected expressions for this group when account is taken of the equation of Gillespie and Coe are given in the following table

Group 18

(Corrected by G> Tune11)

p_9 mj_9 S constant

$$\dot{}_k = -\frac{l_{m_k}}{T} - \breve{S}^k$$

$$(\partial m_k) = (m_1 + \ldots + m_n)\frac{\breve{c}_p}{T}$$

$$(\partial V) = -\frac{\partial S}{\partial m_k}\frac{\partial V}{\partial T} + \frac{\breve{c}_p(m_1 + \ldots + m_n)}{T}\frac{\partial V}{\partial m_k}$$

$$= \left(-\frac{l_{m_k}}{T} - \breve{S}^k\right)\frac{\partial V}{\partial T} + \frac{\breve{c}_p(m_1 + \ldots + m_n)}{T}\frac{\partial V}{\partial m_k}$$

$$(\partial U) = p\frac{\partial S}{\partial m_k}\frac{\partial V}{\partial T} + (m_1 + \ldots + m_n)\frac{\breve{c}_p}{T}\left[\mu_k - p\frac{\partial V}{\partial m_k}\right]$$

$$= p\left(\frac{l_{m_k}}{T} + \breve{S}^k\right)\frac{\partial V}{\partial T} + (m_1 + \ldots + m_n)\frac{\breve{c}_p}{T}\left[\mu_k - p\frac{\partial V}{\partial m_k}\right]$$

$$(\partial G) = \left[S\frac{\partial S}{\partial m_k} + (m_1 + \ldots + m_n)\frac{\breve{c}_p\mu_k}{T}\right]$$

$$= \frac{1}{T}\left[S\left(l_{m_k} + T\breve{S}^k\right) + (m_1 + \ldots + m_n)\breve{c}_p\mu_k\right]$$

$$(\partial H) = \frac{1}{T}(m_1 + \ldots + m_n)\breve{c}_p\mu_k$$

$$(\partial A) = \frac{\partial S}{\partial m_k}\left(S + p\frac{\partial V}{\partial T}\right) + (m_1 + \ldots + m_n)\frac{\breve{c}_p}{T}\left(\mu_k - p\frac{\partial V}{\partial m_k}\right)$$

$$= \frac{1}{T}\left\{\left(l_{m_k} + T\breve{S}^k\right)\left(S + p\frac{\partial V}{\partial T}\right) + (m_1 + \ldots + m_n)\breve{c}_p\left[\mu_k - p\frac{\partial V}{\partial m_k}\right]\right\}$$

$$(\partial W) = p\left(\frac{l_{m_k}}{T} + \breve{S}^k\right)\frac{\partial V}{\partial T} - \frac{\breve{c}_p(m_1 + \ldots + m_n)}{T}p\frac{\partial V}{\partial m_k}$$

$$(\partial Q) = -(m_1 + \ldots + m_n)\breve{c}_p\breve{S}^k$$

In the corrected Table for Group 18, $\check{S}^k$ denotes the specific entropy of pure component k in equilibrium with the multicomponent solution across a semipermeable membrane permeable only to component k.[3] In a good many cases Goranson's expressions involving the term l_{m_k} can be corrected by the substitution of $(l_{m_k} + \check{S}^k)$ for l_{m_k}. However, in some cases this substitution does not make the necessary correction.

In conclusion it may be noted that the principal differences between Goranson's Tables and the present author's Tables are caused by Goranson's erroneous assumption that $\left(\frac{\partial S}{\partial m_k}\right)_{T,p,m_j} = \frac{l_{m_k}}{T}$, m_j denoting all the component masses except m_k, whereas in reality $\left(\frac{\partial S}{\partial m_k}\right)_{T,p,m_j} = \frac{l_{m_k}}{T} + \check{S}^k$ and by Goranson's use of 3n + 3 standard derivatives, whereas in reality all the partial derivatives with respect to the various thermodynamic quantities can be expressed in terms of 3n fundamental derivatives, as Goranson himself recognized.[4]

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[3] It may be noted that the expressions in the table for Group 18 as corrected by the present author are consistent with the expressions in Table IV-22 of this text, although they differ in appearance from the expressions in Table IV-22.

[4] Goranson supplied an auxiliary table (Table A on page 149 of Carnegie Institution of Washington Publication 408) which is intended to permit the expression of the 3n + 3 standard derivatives in terms of 3n fundamental derivatives and the masses of the components. However, Goranson's Table A is also partly invalidated by his incorrect assumption that

$$\left(\frac{\partial S}{\partial m_k}\right)_{T,p,m_j} = \frac{l_{m_k}}{T}.$$

Preface

A collection of thermodynamic formulas for a system of one component and of fixed mass was published by P.W. Bridgman in 1914 in the Physical Revue and an emended and expanded version by him was published by the Harvard University Press in 1925 under the title *A Condensed Collection of Thermodynamic Formulas.* In 1935 A.N. Shaw presented a table of Jacobians for a system of one component and of fixed mass and explained its use in the derivation of thermodynamic relations for such a system in an article entitled "The Derivation of Thermodynamical Relations for a Simple System" published in the Philosophical Transactions of the Royal Society of London. A collection of thermodynamic formulas for multi-component systems of variable total mass by R.W. Goranson appeared in 1930 as Carnegie Institution of Washington Publication No. 408 entitled *Thermodynamical Relations in Multi-Component Systems.* Unfortunately, Goranson had accepted the erroneous assumption made by Sir Joseph Larmor in his obituary notice of Josiah Willard Gibbs (Proceedings of the Royal Society of London, Vol. 75, pp. 280-296, 1905) that the differential of the heat received by an open system is equal to the absolute thermodynamic temperature times the differential of the entropy, $dQ = TdS$. In consequence of this error Goranson's basic equations for the energy and the entropy of a multi-component system are incorrect. In 1933 L.J. Gillespie and J.R. Coe, Jr., in an article published in volume three of the Journal of Chemical Physics showed that in the case of an open system, "the complete variation of the entropy, for simultaneous reversible transfers of heat and mass, is

$$dS = \frac{dq}{T} + \Sigma s_1 dm_1 ."$$

In this equation *dS* denotes the increase in the entropy of the open system, *dq* the amount of heat received by the open system, *T* the absolute thermodynamic temperature, s_x the entropy of unit mass of kind 1 added to the open system, and dm_1 the mass of kind 1 added to the open system. This equation is inconsistent with Goranson's basic equations for the energy and the entropy of a multi-component system and is also inconsistent with very many .expressions in his tables for first and second derivatives in the case of a multi-component system. Gibbs showed in his memoir entitled "On the Equilibrium of Heterogeneous Substances" (Trans. Conn. Acad. of Arts and Sciences, Vol. 3, pp. 108-248 and 343-524, 1874-78) that it is possible to determine the energy and the entropy of a multi-component system by measurements of heat quantities and work quantities in closed systems. On this basis, the present author made a detailed analysis of the measurements necessary to obtain complete thermodynamic information for a binary system of one phase over a given range of temperature, pressure, and composition without involving definitions of heat or work in the case of open systems, which was published in a book entitled *Relations between Intensive Thermodynamic Quantities and Their First Derivatives in a Binary System of One Phase* (W.H. Freeman and Company, 1960.) In this book the present author also presented a table by means of which any desired relation between the absolute thermodynamic temperature *T,* the pressure p, the mass fraction of one component M_1, the specific volume *V,* the specific energy *U,* and the specific entropy *S,* and their first derivatives for a binary system of one phase can be derived from the experimentally determined relations by the use of functional determinants (Jacobians).

In the present work, tables of Jacobians are given for one-component systems of unit mass and of variable mass and for binary systems of unit mass and of variable total mass by means of which relations can be obtained between the thermodynamic quantities and their first derivatives. An explanation of the experimental measurements necessary to obtain complete thermodynamic information in each of these cases is also provided. The table of Jacobians for the case of a one-component system of unit mass is included for comparison with the other tables of Jacobians, because the Jacobians in the tables in the other three cases reduce essentially to those in the table for the case of the one-component system of unit mass when the masses are held constant. The Jacobians in the table in the present text for the case of a one-component system of unit mass are the same as the expressions in Bridgman's tables for this case. The Jacobians in the tables in the present text for the case of a binary system of unit mass differ slightly in form from those in Table 1 of this author's book entitled *Relations between Intensive Thermodynamic Quantities and Their First Derivatives in a Binary System of One Phase.* It has been found that by elimination of the special symbols ξ_1 and σ_1 for $\left(\frac{\partial U}{\partial m_1}\right)_{T,p}$ and $\left(\frac{\partial S}{\partial m_1}\right)_{T,p}$ and adherence to the symbols $\left(\frac{\partial U}{\partial m_1}\right)_{T,p}$ and $\left(\frac{\partial S}{\partial m_1}\right)_{T,p}$ a simpler and more perspicuous arrangement of the terms in the Jacobians results in this case. The Jacobians in the new tables in the present text for the case of a binary system of variable total mass differ very much from the expressions in the tables in Carnegie Institution of Washington Publication No. 408 by R.W. Goranson. Very many of the expressions in Goranson's tables are incorrect on account of his erroneous assumption that *dQ = TdS* in the case of open systems when there is simultaneous reversible transfer of both heat and mass. Furthermore, Goranson's expressions in his tables for first derivatives in such cases are not formulated in terms of the minimum number of derivatives chosen as fundamental as he himself recognized.

As might be expected there is a considerable parallelism between the Jacobians in the tables in the present text for a one-component system of one phase and of variable mass and those in the tables in the present text for a binary system of one phase and of unit mass. There is also a partial parallelism between the Jacobians in the tables in the present text for the two cases just mentioned and those in the present text for the case of a binary system of one phase and of variable total mass. Thus for example in the case of a one-component system of one phase and of variable mass we have

$$\frac{\partial(S, V, U)}{\partial(T, p, M)} = M^2\left\{\left[\breve{U} + p\breve{V} - T\breve{S}\right]\left[\left(\frac{\partial\breve{V}}{\partial T}\right)_p^2 + \frac{\breve{c}_p}{T}\left(\frac{\partial\breve{V}}{\partial p}\right)_T\right]\right\},$$

where 5 denotes the total entropy, *V* the total volume, *U* the total energy, *T* the absolute thermodynamic temperature, *p* the pressure, *M* the mass, $\breve{S}$ the specific entropy, $\breve{V}$ the specific volume, $\breve{U}$ the specific energy, and $\breve{c}_p$ the heat capacity at constant pressure per unit of mass. For comparison in the case of a binary system of one phase and of unit mass we have

$$\frac{\partial(\breve{S}, \breve{V}, \breve{U})}{\partial(T, p, \breve{m}_1)} = \left[\left(\frac{\partial\breve{U}}{\partial\breve{m}_1}\right)_{T, p} + p\left(\frac{\partial\breve{V}}{\partial\breve{m}_1}\right)_{T, p} - T\left(\frac{\partial\breve{S}}{\partial\breve{m}_1}\right)_{T, p}\right]$$

$$\cdot\left[\left(\frac{\partial\breve{V}}{\partial T}\right)_{p, \breve{m}_1}^2 + \frac{\breve{c}_p}{T}\left(\frac{\partial\breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right],$$

Correspondence of Tables of Jacobians

Part I Table 1-1	Part II Tables II-l to 11-15	Part III Tables III-l to 111-15	Part IV Tables IV-1 to IV-35
	1	1	1 & 2
1	2	2	6
	3	3	7 & 10
	4	4	8 & 11
	5	5	9 & 12
1	6	6	16
	7	7	17 & 20
	8	8	18 & 21
	9	9	19 & 22
1	10	10	26
1	11	11	27
1	12	12	28
	13	13	29 & 32
	14	14	30 & 33
	15	15	31 & 34
			3
			4
			5
			13
			14
			15
			23
			24
			25
			35

where $\breve{m}_1$ denotes the mass fraction of component 1, which is equal to m_1, the mass of component 1, divided by the sum of m_1 and m_2t m_2 denoting the mass of component 2.

Furthermore in the case of a binary system of one phase and of variable total mass we have

$$\frac{3(5,\ m_{1t}\ V,\ U)}{3(7\%\ p,\ mi,\ /B2)}$$

$$= -(m_1 + m_2)^2\left\{\left[(\breve{U} + p\breve{V} - T\breve{S}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p}\right)\right] \cdot\left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\,\breve{m}_1} + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right]\right\}.$$

Also we have

$$\frac{3(S,\ 1712,\ F,\ U)}{3(T,\ p,\ mi,\ cia)}$$

$$= (m_1 + m_2)^2\left\{\left[(\breve{U} + p\breve{V} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p}\right)\right] \cdot\left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\,\breve{m}_1} + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right]\right\}.$$

The last factor in each of these four Jacobians is the same. In the case of the next to the last factor in each of these Jacobians there is some parallelism; thus the next to the last factor in the case of the Jacobian $\frac{3(5,\ V,\ U)}{3(T,\ p,\ M)}$ ^s $[\breve{U} + p\breve{V} - T\breve{S}]$ which is equal to the specific Gibbs function $\hat{G}$ or G Mj. The next to the last factor in the case of the

Jacobian $\frac{\partial(\breve{S}, \breve{V}, \breve{U})}{\partial(T, p, \breve{m}_1)}$ is $\left\{\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right\}$

which is equal to $\left(\frac{\partial \breve{G}}{\partial \breve{m}_1}\right)_{T, p}$. Finally the next to the last factor in the case of the Jacobian $\frac{\partial(S, m_2, V, U)}{\partial(T, p, m_1, m_2)}$ is

$$\left[(\breve{U} + p\breve{V} - T\breve{S}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right)\right]$$

which is equal to $\left(\frac{\partial G}{\partial m_2}\right)_{T, p, m_1}$ and the next to the last factor in the case of the Jacobian $\frac{\partial(S, m_1, V, U)}{\partial(T, p, m_1, m_2)}$ is

$$\left[(\breve{U} + p\breve{V} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right)\right]$$

which is equal to $\left(\frac{\partial G}{\partial m_1}\right)_{T, p, m_2}$. It is to be noted that in all of these four Jacobians a simplification would result if use were made of the Gibbs function *G* and its derivatives; however, in the tables this would introduce more first derivatives than the minimum number of fundamental derivatives in terms of which all first derivatives are expressible. If it is merely desired to calculate a particular derivative as the quotient of two Jacobians, the introduction of the Gibbs function *G* (likewise the introduction of the enthalpy, $H \equiv U + pV$, and the Helmholtz function, $A \equiv U - TS$) in the expressions for the Jacobians would cause no difficulty. On the other hand if it is desired to obtain a relation among certain derivatives by expressing them in terms of the minimum number of fundamental derivatives and then eliminating the fundamental derivatives from the equations, the introduction of the Gibbs function *G* (or the enthalpy *H* or the Helmholtz function *A*) in the expressions for the Jacobians would defeat the purpose.

The basic theorem on Jacobians that is needed in the calculation of derivatives of point functions with respect to a new set of independent variables in terms of derivatives with respect to an original set of independent variables was stated by Bryan (in *Encyklopädie der matematischen Wissenschaften,* B.G. Teubner, Leipzig, Bd. V, Teil 1, S. 113, 1903), and is mentioned (without proof) in a number of textbooks on the calculus. Proofs of this theorem in cases of functions of two independent variables and functions of three independent variables are given in Appendix B to Part I and Appendix C to Part II of the present work. In the case of transformations of line integrals that depend upon the path from one coordinate system to another coordinate system, the Jacobian theorem does not apply. To cover this case a new theorem is needed. The new theorem developed by the present author for the expression of the derivatives of a line integral that depends upon the path along lines parallel to the coordinate axes in one plane or space in terms of the derivatives of the line integral along lines parallel to the coordinate axes in other planes or spaces is stated and proved in Appendix B to Part I and Appendix C to Part II of the present work (this theorem is expressed by equations (I-B-36) and (I-B-37) in Appendix B to Part I and equations (II-C-63), (II-C-64), and (II-C-65) in Appendix C to Part II). It is a pleasure to acknowledge my indebtedness to Professor C.J.A. Halberg, Jr., and Professor V.A. Kramer, both of the Department of Mathematics of the University of California at Riverside, who have kindly examined my proof of this theorem carefully and in detail and who have confirmed its correctness. I wish also to express my gratitude to Mrs. Sheila Marshall for carefully and skillfully typing the manuscript of this book in form camera-ready for reproduction by offset photolithography and to Mr. David Crouch for making the drawings for Figures II-l, II-A-1, II-A-2, and IV-A-1.

George Tunell

Santa Barbara, California
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Contents

Part I

Relations between thermodynamic quantities and their first derivatives in a one-component system of one phase and of unit mass

Introduction

In consequence of the first and second laws of thermodynamics and the equation of state of a one-component system of one phase and of unit mass there are very numerous relations between the thermodynamic quantities of such a system and their derivatives. Bridgman[1] devised a table of functions by means of which any first derivative of a thermodynamic quantity of such a system can be evaluated in terms of the three first derivatives, $\left(\frac{\partial \breve{V}}{\partial p}\right)_T$, $\left(\frac{\partial \breve{V}}{\partial T}\right)_p$, and $\breve{C}_p$, together with the absolute thermodynamic temperature and the pressure, as a quotient of two of the tabulated functions. The equation among any four first derivatives can then be obtained by elimination of the three derivatives, $\left(\frac{\partial \breve{V}}{\partial p}\right)_T$, $\left(\frac{\partial \breve{V}}{\partial T}\right)_p$, and $\breve{C}_p$, from the four equations expressing the four first derivatives in terms of the three derivatives, $\left(\frac{\partial \breve{V}}{\partial p}\right)_T$, $\left(\frac{\partial \breve{V}}{\partial T}\right)_p$, and $\breve{C}_p$.

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[1] Bridgman, P.W., Phys. Rev., (2), 3, 273-281, 1914, also *A Condensed Collection of Thermodynamic Formulas,* Harvard University Press, Cambridge, 1925.

Bridgman's table has been found very useful and has become well known. The functions in Bridgman's table can be derived by a simpler method, however. The theorem upon which this method is based had been stated by Bryan,[2] but a proof of this theorem is not included in the article by Bryan. In the following pages the functions tabulated by Bridgman are derived by the method of Jacobians explained by Bryan and the Jacobian theorem is proved.

Equation of state of a one-component system of one phase

The principal properties of a one-component system of one phase and of unit mass that are considered in thermodynamics are the absolute thermodynamic temperature T, the pressure p, the specific volume 7, the specific energy *U,* and the specific entropy 5. It has been established experimentally that the temperature, the pressure, and the specific volume are related by an equation of state

$$*(p, \breve{V}, T) = 0. \qquad (1\text{-}1)$$

Even if an algebraic equation with numerical coefficients cannot be found that will reproduce the experimental data for a particular one-component system within the accuracy of the measurements over the entire range of the measurements, the equation of state can still be represented graphically with such accuracy, and numerical values can be scaled from the graphs.[3]

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[2] Bryan, G.H., in *Encyklopädie der matematischen Missenschaften,* B.G. Teubner, Leipzig, Bd, V, Teil 1, S. 113, 1903.

[3] **Deming, W.E.,** and L.E. Shupe, Phys. Rev., (2), 37, 638-654, 1931; York, Robert, Jr., Industrial and Engineering Chemistry, **32, 54-56,** 1940.

Work done and heat received by the system

One may plot the values of the temperature T and the pressure p of the system in a series of states through which the system passes, laying off the values of T along one coordinate-axis and the values of p along the other coordinate-axis. The points representing the series of states then form a curve, which, following Gibbs[4] one may call the path of the system. As Gibbs further pointed out, the conception of a path must include the idea of direction, to express the order in which the system passes through the series of states. With every such change of state there is connected a certain amount of work, W, done by the system, and a certain amount of heat, Q, received by the system, which Gibbs[5] and Maxwell[6] called the work and the heat of the path. Since the temperature and pressure are supposed uniform throughout the system in any one state, all states are equilibrium states, and the processes discussed are reversible processes.

The work done by this system on the surroundings is expressed mathematically by the equation

$$W = \int_{V_0}^{V} p\,dV. \tag{1-2}$$

[4] Gibbs, J. Willard, Trans. Conn. Acad. of Arts and Sciences, 2, 311, 1871-73, or *Collected Works,* Longmans, Green and Co., New York, 1928, Vol. 1, p. 3.

[5] Gibbs, J. Willard, Trans. Conn. Acad. of Arts and Sciences, 2, 311, 1871-73, or *Collected Works*, Longmans, Green and Co., New York, 1928, Vol. 1, p. 3.

[6] Maxwell, J. Clerk, *Theory of Heat,* 10th Ed., Longmans, Green and Company, London, 1891, p. 186.

The value of this integral depends upon the particular path in the $(p, \breve{V})$-plane, and when the path is determined, for example, by the relation

$$p = f(\breve{V}), \tag{1-3}$$

the value of the integral can be calculated.

If the path is plotted in the (T, p)-plane the work done by the system, W, may be obtained by transformation of the integral in equation (1-2)

$$W = \int_{T_0, p_0}^{T, p} \left\{ p\left(\frac{\partial \breve{V}}{\partial T}\right)_p dT + p\left(\frac{\partial \breve{V}}{\partial p}\right)_T dp \right\} , \tag{1-4}$$

and the path may be determined in this case by the relation

$$p = \phi(T). \tag{1-5}$$

Similarly the heat, Q, received by the system,

$$Q = \int_{T_0, p_0}^{T, p} \left\{ \breve{c}_p dT + \breve{l}_p dp \right\} , \tag{1-6}$$

may be calculated provided the heat capacity at constant pressure per unit of mass, $\breve{c}_p$, and the latent heat of change of pressure at constant temperature per unit of mass, $\breve{l}_p$, are known functions of T and p and the path is determined by equation (1-5). The integrals in equations (1-4) and (1-6) are line integrals[7] that depend upon the particular choice of the path.

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[7] For the definition of a line integral, see W.F. Osgood, *Advanced Calculus,* The Macmillan Company, New York, 1925, pp. 220, 221, or R. Courant, *Differential and Integral Calculus,* translated by J.E. McShane, Blackie & Son, Ltd., London, 1944, Vol. 2, pp. 344, 345.

First and second laws of thermodynamics applied to a one-conponent system of one phase and of unit mass

The first law of thermodynamics for a one-component system of one phase and of unit mass traversing a closed path or cycle is the experimentally established relation

$$\$\{dQ - dW\} = 0. \qquad (1\text{-}7)$$[8]

Replacing $<PdQ$ and $\$dW$ by their values from equations (1-4) and (1-6) in order that the integral may be expressed in terms of the coordinates of the plane in which the path is plotted, one has

$$/\{[*_{\prime\prime} - p(if)_p y \bullet [r_p - p(f)_T]\}dp = 0. \qquad (I\text{-}8)$$

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[8] Blondlot, R., *Introduction a l'Étude de la Thermodynamique*, Gauthier-Villars et Fils, Paris, 1888, p. 66; Bryan, G.H., op. cit., p. 83; Poincare, H., *Thermodynamique*, Second Edition, Edited by J. Blondin, Gauthier-Villars et Cie, Paris, 1923, p. 69; Keenan, J.H., *Thermodynamics,* John Wiley & Sons, Inc., New York, 1941, p. 10; Allis, W.P., and M.A. Herlin, *Thermodynamics and Statistical Mechanics,* McGraw-Hill Book Co., Inc., New York, 1952, p. 67; Schottky, W., H. Ulich, and C. Wagner, *Thermodynamik, die Lehre von den Kreisprozessen, den physikalischen und chemischen Veränderungen und Gleichgewichten,* Julius Springer, Berlin, 1929, pp. 14-15.

Lord Kelvin in his paper entitled *"On* the dynamical theory of heat, with numerical results deduced from Mr. Joule's equivalent of a thermal unit, and M. Regnault's observations on steam" (Trans. Roy. Soc* Edinburgh, 20, 261-288, 1851) made the following statement: "Let us suppose a mass of any substance, occupying a volume v, under a pressure p uniform in all directions, and at a temperature t, to expand in volume to v + dv, and to rise in temperature to t + dt. The quantity of work which it will produce will be

$$pdv;$$

and the quantity of heat which must be added to it to make its temperature rise during the expansion to t + dt may be denoted by

$$Mdv + Ndt,$$

From equation (1-8) it follows that the integral

$$\int_{T_0, p_0}^{T, p} \left\{ \left[\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_p \right] dT + \left[\breve{l}_p - p\left(\frac{\partial \breve{V}}{\partial p}\right)_T \right] dp \right\}$$

is independent of the path and defines a function of the

The mechanical equivalent of this is

$$J(Mdv + Ndt),$$

if J denote the mechanical equivalent of a unit of heat. Hence the mechanical measure of the total external effect produced in the circumstances is

$$(p - JM)dv - JNdt.$$

The total external effect, after any finite amount of expansion, accompanied by any continuous change of temperature, has taken place, will consequently be, in mechanical terms,

$$\int\{(p - JM)dv - JNdt\} ;$$

where we must suppose t to vary with v, so as to be the actual temperature of the medium at each instant, and the integration with reference to v must be performed between limits corresponding to the initial and final volumes. Now if, at any subsequent time, the volume and temperature of the medium become what they were at the beginning, however arbitrarily they may have been made to vary in the period, the total external effect must, according to Prop. I., amount to nothing; and hence

$$(p - JM)dv - JNdt$$

must be the differential of a function of two independent variables, or we must have

$$\frac{d(p - JM)}{dt} = \frac{d(-JN)}{dv} \qquad (1),$$

this being merely the analytical expression of the condition, that the preceding integral may vanish in every case in which the initial and final values of v and t are the same, respectively." And elsewhere in the same paper Lord Kelvin wrote: "Prop, I. (Joule).-When equal quantities of mechanical effect are produced by any means whatever, from purely thermal sources, or lost in purely thermal effects, equal quantities of heat are put out of existence or are generated."[1]

coordinates; this function, to which the name energy is given and which is here denoted by the letter *U,* is thus a function of the state of the system

$\breve{U}(T, p) - \breve{U}(T_0, p_0) =$

Kb - '$)>• & - 4\] 4 • (H>)

^{r}o» Po

The second law of thermodynamics for a one-component system of one phase and of unit mass traversing a closed reversible path or cycle is the experimentally established relation

$$\oint f\text{-} = 0\ ,[9] \qquad (1\text{-}10)$$

where *T* is the temperature on the absolute thermodynamic scale. Expressing this integral in terms of the coordinates of the plane in which the path is plotted, one has

$$\oint \left\{ \frac{\breve{c}_p}{T}\, dT + \frac{\breve{l}_p}{T}\, dp \right\} = 0\ . \qquad (\text{I-ll})$$

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[9] Clausius, R., Die *mechanische Wärmetheorie*$_f$ Dritte aufl., Bd. I, Friedrich Vieweg und Sohn, Braunschweig, 1887, S. 93; Blondlot, R., op. **cit.,** p. 66; **Van^{f}t** Hoff, J.H., *Physical Chemistry in the Service of the Sciences*$_9$ English Version by A. Smith, University of Chicago Press, Chicago, 1903, pp. 21-22; Schottky, W., H. Ulich, and C. Wagner, op. cit., p. 17; Gibbs, J. Willard, Proceedings of the American Academy of Arts and Sciences, new series, 16, 460, 1889, or *Collected Works,* Vol. 2, Longmans, Green and Company, New York, 1928, p. 263.

From equation (1-11) it follows that the integral

$$\int_{T_o,\, p_o}^{T,\, p} \left\{ \frac{\breve{c}_p}{T} dT + \frac{\breve{l}_p}{T} dp \right\}$$

is independent of the path and defines a function of the coordinates; this function, to which the name entropy is given and which is here denoted by the letter $\breve{S}$, is thus a function of the state of the system

$$\breve{S}(T,p) - \breve{S}(T_o,p_o) = \int_{T_o,\, p_o}^{T,\, p} \left\{ \frac{\breve{c}_p}{T} dT + \frac{\breve{l}_p}{T} dp \right\}. \qquad \text{(I-12)}$$

From equation (1-9) it follows directly[10] that

$$\left(\frac{\partial \breve{U}}{\partial T}\right)_p = \breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_p \qquad \text{(I-13)}$$

and

$$\left(\frac{\partial \breve{U}}{\partial p}\right)_T = \breve{l}_p - p\left(\frac{\partial \breve{V}}{\partial p}\right)_T . \qquad \text{(I-14)}$$

From equation (1-12) it follows likewise that

$$\left(\frac{\partial \breve{S}}{\partial T}\right)_p = \frac{\breve{c}_p}{T} \qquad \text{(I-15)}$$

and

$$\left(\frac{\partial \breve{S}}{\partial p}\right)_T = \frac{\breve{l}_p}{T} . \qquad \text{(I-16)}$$

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[10] For the proof of this theorem, see W.F. Osgood, op. cit., pp. 229-230, or R. Courant - J.E. McShane, op. cit., Vol. 1, pp. 352-355.

A necessary and sufficient condition[11] for equation (1-9) to be true is

$$\left\{\frac{\partial\left[l_p - p\left(\frac{\partial v}{\partial p}\right)_T\right]}{\partial T}\right\}_p = \left\{\frac{\partial\left[c_p - p\left(\frac{\partial v}{\partial T}\right)_p\right]}{\partial p}\right\}_T . \quad ^{12} \tag{1-17}$$

Likewise a necessary and sufficient condition for equation (1-12) to be true is

$$\left\{\frac{\partial \frac{l_p}{T}}{\partial T}\right\}_p = \left\{\frac{\partial \frac{c_p}{T}}{\partial p}\right\}_T . \quad ^{13} \tag{1-18}$$

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[11] For the proof of this theorem, see W.F. Osgood, op. cit., pp. 228-230, or R. Courant - J.E. McShane, op. cit., Vol. 1, pp. 352-355.

[12] Lord Kelvin wrote the analogous equation with t and v as the independent variables as an analytical expression of the "first fundamental proposition" or first law of thermodynamics. His statement follows: "Observing that J is an absolute constant, we may put the result into the form

$$\frac{dp}{dt} = J\left(\frac{dM}{dt} - \frac{dN}{dv}\right).$$

This equation expresses, in a perfectly comprehensive manner, the application of the first fundamental proposition to the thermal and mechanical circumstances of any substance whatever, under uniform pressure in all directions, when subjected to any possible variations of temperature, volume, and pressure." (Trans. Roy. Soc. Edinburgh, 20, 270, 1851.) Clausius also stated that an analogous equation, his equation (5), forms an analytical expression of the first law for reversible changes in a system the state of which is determined by two independent variables. (*Abhandlungen über die mechanische Wärmetheorie*, Zweite Abtheilung, Abhandlung IX, Friedrich Vieweg und Sohn, Braunschweig, 1867, p. 9.)

[13] Clausius stated that his equation (6), to which equation (1-18) of this text is analogous, constituted an analytical expression of the second law for reversible processes in a system the state of which is determined by two independent variables. (*Abhandlungen über die mechanische Wärmetheorie*, Zweite Abtheilung, Abhandlung IX, Friedrich Vieweg und Sohn, Braunschweig, 1867, p. 9.)

Carrying out the indicated differentiations one obtains from equation (1-17) the relation

$$\left(\frac{\partial \breve{l}_p}{\partial T}\right)_p - p\frac{\partial^2 \breve{V}}{\partial T \partial p} = \left(\frac{\partial \breve{c}_p}{\partial p}\right)_T - p\frac{\partial^2 \breve{V}}{\partial p \partial T} - \left(\frac{\partial \breve{V}}{\partial T}\right)_p \qquad (1\text{-}19)$$

and from equation (1-18) the relation

$$\frac{1}{T}\left(\frac{\partial \breve{l}_p}{\partial T}\right)_p - \frac{\breve{l}_p}{T^2} = \frac{1}{T}\left(\frac{\partial \breve{c}_p}{\partial p}\right)_T \quad . \qquad (1\text{-}20)$$

Combining equations (1-19) and (1-20) one has

$$\breve{l}_p = -T\left(\frac{\partial \breve{V}}{\partial T}\right)_p \quad . \qquad (1\text{-}21)$$

From equations (1-19) and (1-21) it also follows that

$$\left(\frac{\partial \breve{c}_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 \breve{V}}{\partial T^2}\right)_p \quad . \qquad (1\text{-}22)$$

All the first derivatives of the three quantities *V*, *U** and *S* expressed as functions of *T* and p can thus be calculated from equations (1-13), (1-14), (1-15), (1-16), and (1-21) if $\left(\frac{\partial V}{\partial T}\right)_p$, $\left(\frac{\partial V}{\partial p}\right)_T$, and c_p have been determined experimentally.

In order to be able to calculate all the properties of this system at any temperature and pressure, the volume must be determined experimentally as a function of the temperature and pressure; the first two derivatives $\left(\frac{\partial V}{\partial T}\right)_p$ and $\left(\frac{\partial V}{\partial p}\right)_T$ can then be calculated at any temperature and pressure within the range over which the volume has been determined. The third derivative, c_p, need only be determined experimentally along some line not at constant temperature,[14] since $\left(\frac{\partial c_p}{\partial p}\right)_T$ can be calculated from equation (1-22) if $\left(\frac{\partial V}{\partial T}\right)_p$ has been determined as a function of T and p.

Derivation of any desired relation between the intensive thermodynamic quantities, T, p, V, U, S, and their first derivatives for a one-component system of one phase from the experimentally determined relations by the use of functional determinants (Jacobians)

Equations (1-1), (1-9), and (1-12) can be solved for any three of the quantities, T, p, V, U, S as functions of the remaining two. The first partial derivative of any one of the quantities, T, p, V, U, S with respect to any second quantity when any third quantity is held constant can readily be obtained in terms of the three first derivatives $\left(\frac{\partial V}{\partial T}\right)_p$, $\left(\frac{\partial V}{\partial p}\right)_T$, and c_p, together with the absolute thermodynamic temperature and the pressure, by application of the theorem stating that if $x' = \varphi(x, y)$, if $x = f(u, v)$, and if $y = \psi(u, v)$, then one has

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[14] Bridgman, P.W., Phys, Rev., (2), 3, 274, 1914.

$$\left(\frac{\partial x'}{\partial x}\right)_y = \frac{\begin{vmatrix} \left(\frac{\partial x'}{\partial u}\right)_v & \left(\frac{\partial x'}{\partial v}\right)_u \\ \left(\frac{\partial y}{\partial u}\right)_v & \left(\frac{\partial y}{\partial v}\right)_u \end{vmatrix}}{\begin{vmatrix} \left(\frac{\partial x}{\partial u}\right)_v & \left(\frac{\partial x}{\partial v}\right)_u \\ \left(\frac{\partial y}{\partial u}\right)_v & \left(\frac{\partial y}{\partial v}\right)_u \end{vmatrix}} = \frac{\frac{\partial(x', y)}{\partial(u, v)}}{\frac{\partial(x, y)}{\partial(u, v)}} \quad (1\text{-}23)$$

[15]

provided all the partial derivatives in the determinants are continuous and provided the determinant in the denominator is not equal to zero. The symbol $\frac{\partial(x', y)}{\partial(u, v)}$ here denotes the Jacobian[16] of the functions x' and y with respect to the variables u and v and the symbol $\frac{\partial(x, y)}{\partial(u, v)}$ denotes the Jacobian of the functions x and y with respect to the variables u and v. In Table 1-1 the value of the Jacobian is given for each pair of the variables, T, p, V, U, S, as x', y or x, y and

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[15] Bryan, G.H., op. cit., p. 113, equation (82); see also Osgood, W.F., op. cit., p. 150, Exercise 31, Burington, R.S., and C.C. Torrance. *Higher Mathematics with Applications to Science and Engineering*, McGraw-Hill Book Co., Inc., New York and London, 1939, p. 138, Exercise 7, and Sherwood, T.K., and C.E. Reed, *Applied Mathematics in Chemical Engineering*, McGraw-Hill Book Co., Inc., New York and London, 1939, p. 174, equation (164). A proof of this theorem for the case of functions of two independent variables is given in Appendix B to Part I.

[16] For the definition of a Jacobian, see W.B. Fite, *Advanced Calculus*, The Macmillan Company, New York, 1938, pp. 308-309.

with T, p as u, v. There are 20 Jacobians in the table, but one has $\frac{\partial(x, y)}{\partial(u, v)} = -\frac{\partial(y, x)}{\partial(u, v)}$, because interchanging the rows of the determinant changes the sign of the determinant; hence it is only necessary to calculate the values of 10 of the determinants. The calculations of these ten determinants follow:

$$\frac{\partial(p, T)}{\partial(T, p)} = \begin{vmatrix} \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} \end{vmatrix} = -1 ; \tag{1-24}$$

$$\frac{\partial(\breve{V}, T)}{\partial(T, p)} = \begin{vmatrix} \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} \end{vmatrix} = -\left(\frac{\partial \breve{V}}{\partial p}\right)_T ; \tag{1-25}$$

$$\frac{\partial(\breve{E}, T)}{\partial(T, p)} = \begin{vmatrix} \frac{\partial \breve{E}}{\partial T} & \frac{\partial \breve{E}}{\partial p} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} \end{vmatrix} = T\left(\frac{\partial \breve{V}}{\partial T}\right)_p + p\left(\frac{\partial \breve{V}}{\partial p}\right)_T ; \tag{1-26}$$

$$\frac{\partial(\breve{S}, T)}{\partial(T, p)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} \end{vmatrix} = \left(\frac{\partial \breve{V}}{\partial T}\right)_p ; \tag{1-27}$$

$$\frac{\partial(\breve{V}, p)}{\partial(T, p)} = \begin{vmatrix} \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} \end{vmatrix} = \left(\frac{\partial \breve{V}}{\partial T}\right)_p ; \tag{1-28}$$

$$\frac{\partial(\breve{U}, p)}{\partial(T, p)} = \begin{vmatrix} \dfrac{\partial \breve{U}}{\partial T} & \dfrac{\partial \breve{U}}{\partial p} \\[2ex] \dfrac{\partial p}{\partial T} & \dfrac{\partial p}{\partial p} \end{vmatrix} = \breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_p ; \tag{1-29}$$

$$\frac{\partial(\breve{S}, p)}{\partial(T, p)} = \begin{vmatrix} \dfrac{\partial \breve{S}}{\partial T} & \dfrac{\partial \breve{S}}{\partial p} \\[2ex] \dfrac{\partial p}{\partial T} & \dfrac{\partial p}{\partial p} \end{vmatrix} = \frac{\breve{c}_p}{T} ; \tag{1-30}$$

$$\frac{\partial(\breve{U}, \breve{V})}{\partial(T, p)} = \begin{vmatrix} \dfrac{\partial \breve{U}}{\partial T} & \dfrac{\partial \breve{U}}{\partial p} \\[2ex] \dfrac{\partial \breve{V}}{\partial T} & \dfrac{\partial \breve{V}}{\partial p} \end{vmatrix} = T\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \breve{c}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_T ; \tag{1-31}$$

$$\frac{\partial(\breve{S}, \breve{V})}{\partial(T, p)} = \begin{vmatrix} \dfrac{\partial \breve{S}}{\partial T} & \dfrac{\partial \breve{S}}{\partial p} \\[2ex] \dfrac{\partial \breve{V}}{\partial T} & \dfrac{\partial \breve{V}}{\partial p} \end{vmatrix} = \left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T ; \tag{1-32}$$

$$\frac{\partial(\breve{S}, \breve{U})}{\partial(T, p)} = \begin{vmatrix} \dfrac{\partial \breve{S}}{\partial T} & \dfrac{\partial \breve{S}}{\partial p} \\[2ex] \dfrac{\partial \breve{U}}{\partial T} & \dfrac{\partial \breve{U}}{\partial p} \end{vmatrix} = -p\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 - \frac{p\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T . \tag{1-33}$$

In order to obtain the first partial derivative of any one of the five quantities T, p, $\breve{V}$, $\breve{U}$, $\breve{S}$ with respect to any second quantity of the five when any third quantity of the five is held constant, one has only to divide the value of the **Jacobian** in Table 1-1 in which the first letter in the first line is the quantity being differentiated and in which the second letter in the first line is the quantity held constant

Table 1-1
Jacobians of intensive functions for a one-component system of one phase

$$\frac{\partial(x', y)}{\partial(T, P)}, \quad \frac{\partial(x, y)}{\partial(T, P)}$$

$x \setminus y$	T	P	$\breve{V}$	$\breve{U}$	$\breve{S}$
T	~	1	$\left(\frac{\partial \breve{V}}{\partial P}\right)_T$	[illegible]	$-\left(\frac{\partial \breve{V}}{\partial T}\right)_P$
P	-1	~	$-\left(\frac{\partial \breve{V}}{\partial T}\right)_P$	$-\breve{C}_P + P\left(\frac{\partial \breve{V}}{\partial T}\right)_P$	$-\frac{\breve{C}_P}{T}$
$\breve{V}$	$-\left(\frac{\partial \breve{V}}{\partial P}\right)_T$	$\left(\frac{\partial \breve{V}}{\partial T}\right)_P$	~	$-T\left(\frac{\partial \breve{V}}{\partial T}\right)_P^2 - \breve{C}_P\left(\frac{\partial \breve{V}}{\partial P}\right)_T$	[illegible]
$\breve{U}$	$T\left(\frac{\partial \breve{V}}{\partial T}\right)_P + P\left(\frac{\partial \breve{V}}{\partial P}\right)_T$	$\breve{C}_P - P\left(\frac{\partial \breve{V}}{\partial T}\right)_P$	[illegible]	~	$P\left(\frac{\partial \breve{V}}{\partial T}\right)_P^2 + \frac{P\breve{C}_P}{T}\left(\frac{\partial \breve{V}}{\partial P}\right)_T$
$\breve{S}$	$\left(\frac{\partial \breve{V}}{\partial T}\right)_P$	$\frac{\breve{C}_P}{T}$	$\left(\frac{\partial \breve{V}}{\partial T}\right)_P^2 + \frac{\breve{C}_P}{T}\left(\frac{\partial \breve{V}}{\partial P}\right)_T$	$-P\left(\frac{\partial \breve{V}}{\partial T}\right)_P^2 - \frac{P\breve{C}_P}{T}\left(\frac{\partial \breve{V}}{\partial P}\right)_T$	~

by the value of the Jacobian in Table 1-1 in which the first letter of the first line is the quantity with respect to which the differentiation is taking place and in which the second letter in the first line is the quantity held constant.

To obtain the relation among any four derivatives, having expressed them in terms of the same three derivatives, $\left(\frac{\partial V}{\partial T}\right)_p$, $\left(\frac{\partial V}{\partial p}\right)_T$, and c_p, one has only to eliminate the three derivatives from the four equations, leaving a single equation connecting the four derivatives.

Three functions used in thermodynamics to facilitate the solution of many problems are the following: the enthalpy H, defined by the equation $H \equiv U + pV$, the Helmholtz function A, defined by the equation $A \equiv U - TS$, and the Gibbs function G, defined by the equation $G \equiv U + pV - TS$. The corresponding specific functions are H, A, and G. Partial derivatives involving one or more of the functions H, A, and G, can also be calculated as the quotients of two Jacobians, which can themselves be calculated by the same method used to calculate the Jacobians in Table 1-1.

Appendix A to Part I

Transformation of the work and heat line integrals from one coordinate plane to other coordinate planes in the case of a one-component system of one phase and of unit mass

The derivatives of the work done and the heat received by a one-component system of one phase and of unit mass are total derivatives[1] with respect to the variables chosen as the parameters defining the paths of the integrals. In order to obtain the total derivative of the work done along a straight line parallel to one of the coordinate axes in any plane, one obtains from Table 1-1 the partial derivative of the volume with respect to the quantity plotted along that axis when the quantity plotted along the other axis is held constant and one multiplies the partial derivative of the volume by the pressure. Similarly to obtain the total derivative of the heat received along a straight line parallel to one of the coordinate axes in any plane, one obtains from the table the partial derivative of the entropy with respect to the quantity plotted along that axis when the quantity plotted along the other axis is held constant and one multiplies the partial derivative of the entropy by the temperature. For example, the derivatives of the work done and heat received along a straight line parallel to the K-axis in the (7\ **7)-plane** are

$$(\S)_T - P \qquad (I-A-D$$

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[1] **Tunell,** G., Jour. Chenu Physics, 9, 191-192, 1941,

and

$1= KDJ* (II- (I-A-2)

The total derivatives of the heat received along lines parallel to the coordinate axes in any desired plane can also be derived in terms of the total derivatives of the heat received along lines parallel to the coordinate axes in the (T, p)-plane by transformation of the heat line integral as explained in the second half of Appendix B to Part I. Following is an example of such a transformation. In the case of a one-component system of one phase and of unit mass the heat line integral extended along a path in the $(T, \breve{V})$-plane is

$$Q = \int_{T_0, \breve{V}_0}^{T, \breve{V}} \left\{ \left(\frac{dQ}{dT}\right)_{\breve{V}} dT + \left(\frac{dQ}{d\breve{V}}\right)_T d\breve{V} \right\}$$

$$= \int_{T_0, \breve{V}_0}^{T, \breve{V}} \left\{ \qquad + l_v d\breve{V} \right\}, \qquad \text{(I-A-3)}$$

where $\breve{c}_v$ denotes the heat capacity at constant volume per unit of mass and l_v denotes the latent heat of change of volume at constant temperature, and where $\breve{c}_v$ and l_v are functions of T and $\breve{V}$. This integral depends upon the path in the $(T, \breve{V})$-plane determined by an equation between T and $\breve{V}$, $T = f(\breve{V})$.

In this case $\left(\frac{\partial l_v}{\partial T}\right)_{\breve{V}} \neq \left(\frac{\partial \breve{c}_v}{\partial \breve{V}}\right)_T$. In order to transform the integral for Q from the $(T, \breve{V})$-plane to the (T, p)-plane, p denoting the pressure, we make use of the fact that $\breve{V}$ is a function of T and p,

$$\breve{V} = F(T, p). \tag{I-A-4}$$

Thus we write for the integral transposed to the (T, p)-plane

$$Q = \int_{T_0, p_0}^{T, p} \left\{ \breve{c}_V dT + l_V \left(\left(\frac{\partial \breve{V}}{\partial T}\right)_p dT + \left(\frac{\partial \breve{V}}{\partial p}\right)_T dp \right) \right\}$$

$$= \int_{T_0, p_0}^{T, p} \left\{ \left(\breve{c}_V + l_V \left(\frac{\partial \breve{V}}{\partial T}\right)_p \right) dT + l_V \left(\frac{\partial \breve{V}}{\partial p}\right)_T dp \right\} . \tag{I-A-5}$$

By definition the coefficients of dT and dp in this integral are $\breve{c}_p$ and $\breve{l}_p$. Thus we obtain the equations

$$\breve{c}_p = \breve{c}_V + l_V \left(\frac{\partial \breve{V}}{\partial T}\right)_p \tag{I-A-6}$$

and

$$\breve{l}_p = l_V \left(\frac{\partial \breve{V}}{\partial p}\right)_T . \tag{I-A-7}$$

From equations (I-A-6) and (I-A-7) we obtain $\breve{c}_V$ and l_V as functions of T and p:

$$\breve{c}_V = \breve{c}_p - \breve{l}_p \left(\frac{\partial \breve{V}}{\partial T}\right)_p \bigg/ \left(\frac{\partial \breve{V}}{\partial p}\right)_T \tag{I-A-8}$$

and

$$l_V = \breve{l}_p \bigg/ \left(\frac{\partial \breve{V}}{\partial p}\right)_T . \tag{I-A-9}$$

The same result can be obtained by substitution of values in equations (I-B-35) and (I-B-36) in Appendix B to Part I. The equivalence of symbols for the purpose of this substitution is given in the following Table.

Table I-A-l
Equivalence of symbols

r	o
x	T
y	$\breve{V}$
$P(x, y)$	$\left(\frac{dQ}{dT}\right)_{\breve{V}}$
$Q(x, y)$	$\left(\frac{dQ}{d\breve{V}}\right)_T$
u	T
v	p
$\theta(u, v)$	$\breve{c}_p$
tt(u,v)	L_p

Substituting the values from the right hand column for the values in the left hand column in equations (I-B-35) and

(I-B-36) we have

$$\left(\frac{dQ}{dT}\right)_{\breve V} = \breve{c}_V = \frac{\breve{c}_p\left(\frac{\partial \breve V}{\partial p}\right)_T - \breve{l}_p\left(\frac{\partial \breve V}{\partial T}\right)_p}{\left(\frac{\partial \breve V}{\partial p}\right)_T}$$

$$= \left[\breve{c}_p\left(\frac{\partial \breve V}{\partial p}\right)_T + T\left(\frac{\partial \breve V}{\partial T}\right)_p^2\right] \div \left(\frac{\partial \breve V}{\partial p}\right)_T , \qquad \text{(I-A-10)}$$

and

$$\left(\frac{dQ}{d\breve V}\right)_T = \breve{l}_V = \frac{\breve{c}_p \cdot 0 - \breve{l}_p \cdot 1}{\left(\frac{\partial \breve V}{\partial T}\right)_p \cdot 0 - \left(\frac{\partial \breve V}{\partial p}\right)_T \cdot 1}$$

$$= \left[-T\left(\frac{\partial \breve V}{\partial T}\right)_p\right] \div \left(\frac{\partial \breve V}{\partial p}\right)_T . \qquad \text{(I-A-11)}$$

Finally, equations (I-A-8) and (I-A-10) are equivalent because

$$\breve{l}_p = -T\left(\frac{\partial \breve V}{\partial T}\right)_p .$$

Appendix B to Part I

Proofs of the relations:

$$\left(\frac{\partial x'}{\partial x}\right)_y = \frac{\dfrac{\partial(x', y)}{\partial(u, v)}}{\dfrac{\partial(x, y)}{\partial(u, v)}}$$

and

$$\left(\frac{\partial x'}{\partial x}\right)_y = \frac{\begin{vmatrix} \dfrac{\partial x'}{\partial u} & \dfrac{\partial x'}{\partial v} \\ \dfrac{\partial y}{\partial u} & \dfrac{\partial y}{\partial v} \end{vmatrix}}{\begin{vmatrix} \dfrac{\partial x}{\partial u} & \dfrac{\partial x}{\partial v} \\ \dfrac{\partial y}{\partial u} & \dfrac{\partial y}{\partial v} \end{vmatrix}}$$

It is assumed that x' is a function of x and y,

$$x' = \omega(x, y) \qquad \text{(I-B-1)}$$

and that x and y are functions of u and v,

$$x = f(u, v), \qquad \text{(I-B-2)}$$

and

$$y = \theta(u, v). \qquad \text{(I-B-3)}$$

It is assumed further that these functions are continuous together with their first partial derivatives. By application of the theorem for change of variables in partial differentiation[1] one then obtains

$$\frac{\partial x'}{\partial u} = \frac{\partial x'}{\partial x}\frac{\partial x}{\partial u} + \frac{\partial x'}{\partial y}\frac{\partial y}{\partial u} \qquad \text{(I-B-4)}$$

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[1] Osgood, W.F., *Advanced Calculus,* The MacMillan Co., New York, 1925, pp. 112-115; Taylor, Angus, *Advanced Calculus,* Ginn and Co., Boston, New York, Chicago, Atlanta, Dallas, Palo Alto, Toronto, London, 1955, pp. 167-172.

and

$$\frac{\partial x'}{\partial v} = \frac{\partial x'}{\partial x}\frac{\partial x}{\partial v} + \frac{\partial x'}{\partial y}\frac{\partial y}{\partial v} \; . \qquad \text{(I-B-5)}$$

From equations (I-B-4) and (I-B-5) it follows that

$$\frac{\partial x'}{\partial y}\frac{\partial y}{\partial u} = \frac{\partial x'}{\partial u} - \frac{\partial x'}{\partial x}\frac{\partial x}{\partial u} \qquad \text{(I-B-6)}$$

and

$$\frac{\partial x'}{\partial y}\frac{\partial y}{\partial v} = \frac{\partial x'}{\partial v} - \frac{\partial x'}{\partial x}\frac{\partial x}{\partial v} \; . \qquad \text{(I-B-7)}$$

Dividing both sides of equation (I-B-6) by $\frac{\partial y}{\partial u}$ and both sides of equation (I-B-7) by $\frac{\partial y}{\partial v}$ we have

$$\frac{\partial x'}{\partial y} = \frac{\frac{\partial x'}{\partial u} - \frac{\partial x'}{\partial x}\frac{\partial x}{\partial u}}{\frac{\partial y}{\partial u}} \qquad \text{(I-B-8)}$$

and

$$\frac{\partial x'}{\partial y} = \frac{\frac{\partial x'}{\partial v} - \frac{\partial x'}{\partial x}\frac{\partial x}{\partial v}}{\frac{\partial y}{\partial v}} \; . \qquad \text{(I-B-9)}$$

It follows that the right side of equation (I-B-8) is equal to the right side of equation (I-B-9)

$$\frac{\frac{\partial x'}{\partial u} - \frac{\partial x'}{\partial x}\frac{\partial x}{\partial u}}{\frac{\partial y}{\partial u}} = \frac{\frac{\partial x'}{\partial v} - \frac{\partial x'}{\partial x}\frac{\partial x}{\partial v}}{\frac{\partial y}{\partial v}} \; . \qquad \text{(I-B-10)}$$

Multiplying both sides of equation (I-B-10) by $\left(\frac{\partial y}{\partial v}\right)$ we have

$$\frac{\partial y}{\partial v}\left(\frac{\partial x'}{\partial u} - \frac{\partial x'}{\partial x}\frac{\partial x}{\partial u}\right) = \frac{\partial y}{\partial u}\left(\frac{\partial x'}{\partial v} - \frac{\partial x'}{\partial x}\frac{\partial x}{\partial v}\right) \qquad \text{(I-B-11)}$$

and consequently

$$\frac{\partial y}{\partial v}\frac{\partial x'}{\partial u} - \frac{\partial y}{\partial v}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial u} = \frac{\partial y}{\partial u}\frac{\partial x'}{\partial v} - \frac{\partial y}{\partial u}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial v} . \qquad \text{(I-B-12)}$$

From equation (I-B-12) it follows that

$$\frac{\partial x'}{\partial x}\frac{\partial y}{\partial u}\frac{\partial x}{\partial v} - \frac{\partial x'}{\partial x}\frac{\partial y}{\partial v}\frac{\partial x}{\partial u} = \frac{\partial y}{\partial u}\frac{\partial x'}{\partial v} - \frac{\partial y}{\partial v}\frac{\partial x'}{\partial u} \qquad \text{(I-B-13)}$$

and

$$\frac{\partial x'}{\partial x}\left(\frac{\partial y}{\partial u}\frac{\partial x}{\partial v} - \frac{\partial y}{\partial v}\frac{\partial x}{\partial u}\right) = \frac{\partial y}{\partial u}\frac{\partial x'}{\partial v} - \frac{\partial y}{\partial v}\frac{\partial x'}{\partial u} . \qquad \text{(I-B-14)}$$

Dividing both sides of equation (I-B-14) by $\left(\frac{\partial y}{\partial u}\frac{\partial x}{\partial v} - \frac{\partial y}{\partial v}\frac{\partial x}{\partial u}\right)$ we have

$$\left(\frac{\partial x'}{\partial x}\right)_y = \frac{\frac{\partial y}{\partial u}\frac{\partial x'}{\partial v} - \frac{\partial y}{\partial v}\frac{\partial x'}{\partial u}}{\frac{\partial y}{\partial u}\frac{\partial x}{\partial v} - \frac{\partial y}{\partial v}\frac{\partial x}{\partial u}} . \qquad \text{(I-B-15)}$$

The partial derivative $\left(\frac{\partial x'}{\partial x}\right)_y$ is thus equal to the quotient of two Jacobian determinants

$$\left(\frac{\partial x'}{\partial x}\right)_y = \frac{\begin{vmatrix} \frac{\partial x'}{\partial u} & \frac{\partial x'}{\partial v} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} \end{vmatrix}}{\begin{vmatrix} \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} \end{vmatrix}} , \qquad \text{(I-B-16)}$$

provided the Jacobian determinant in the denominator is not equal to zero. Thus we obtain the result

$$\left(\frac{\partial x'}{\partial x}\right)_y = \frac{\frac{\partial(x', y)}{\partial(u, v)}}{\frac{\partial(x, y)}{\partial(u, v)}} \qquad \text{(I-B-17)}$$

and similarly we have

$$\left(\frac{\partial x'}{\partial y}\right)_x = \frac{\frac{\partial(x', x)}{\partial(u, v)}}{\frac{\partial(y, x)}{\partial(u, v)}} . \qquad \text{(I-B-18)}$$

This case corresponds to the case of a one-component system of one phase and of unit mass in which it is desired to transform a function of the coordinates, such as the volume, the energy, or the entropy, from one coordinate plane, such as the entropy-volume plane to another coordinate plane, such as the temperature-pressure plane.

Equations (I-B-17) and **(I-B-18)** are not applicable, however, in the case of a one-component system of one phase and of unit mass when it is desired to transform the work line integral or the heat line integral from one coordinate plane, such as the entropy-volume plane, to another coordinate plane, such as the temperature-pressure plane, because the work line integral and the heat line integral depend upon the path and are not functions of the coordinates. In this case, to which the second equation of the heading of this Appendix applies, the transformation can be accomplished in the following way. Let us suppose that a line integral Γ

$$\Gamma = \int_{x_0, y_0}^{x, y} (P(x, y)dx + Q(x, y)dy) \qquad \text{(I-B-19)}$$

depends upon the path in which case $\frac{\partial P}{\partial y} \neq \frac{\partial Q}{\partial x}$. This integral has no meaning unless a further relation is given between x and y, $y = f(x)$, defining a particular path in the (x, y)-plane.[2] We are next given that x and y are functions of u and v,

$$x = \phi(u, v), \qquad \text{(I-B-20)}$$

and

$$y = \psi(u, v). \qquad \text{(I-B-21)}$$

It is then desired to transform the integral Γ from the

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[2] In general this curve can be represented in parametric form, $x = \chi(\sigma)$, $y = \zeta(\sigma)$, but in simple cases the curve can be expressed by the equation $y = f(x)$, or at least in segments by the equations $y^{I} = f(x)$, $y^{II} = F(x)$.

(x, y)-plane to the (u, v)-plane.[3] In this case if equations (I-B-20) and (I-B-21) can be solved so that we have

$$u = \Phi(x, y), \tag{I-B-22}$$

and

$$v = \Psi(x, y), \tag{I-B-23}$$

then the curve in the (x, y)-plane can be transformed into the curve in the (u, v)-plane defined by the equation $u = F(v)$.

We next replace dx in the integral T by $\frac{\partial x}{\partial u}du + \frac{\partial x}{\partial v}dv$ and dy by $\frac{\partial y}{\partial u}du + \frac{\partial y}{\partial v}dv$. We then have

$$T = \int_{u_0, v_0}^{u, v} \left\{ P\left[\frac{\partial x}{\partial u}du + \frac{\partial x}{\partial v}dv\right] + Q\left[\frac{\partial y}{\partial u}du + \frac{\partial y}{\partial v}dv\right]\right\}, \tag{I-B-24}$$

the curve in the (u, v)-plane now being determined by the

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[3] Cf. R. Courant, *Differential and Integral Calculus,* Translated by J.E. McShane, Blackie & Son Ltd., London and Glasgow, 1944, Vol. 2, p. 373. The procedure for transforming a line integral that depends upon the path from the (x, y)-plane to the (u, v)-plane used by Courant is the same as the procedure explained here and in Appendix C to Part II of this text.

equation $u = F(v)$. Consequently we thus obtain

$$\Gamma = \int_{u_0, v_0}^{u, v} \left\{ P(\phi(u, v), \psi(u, v)) \left[\frac{\partial x}{\partial u} du + \frac{\partial x}{\partial v} dv \right] \right.$$

$$\left. + Q(\phi(u, v), \psi(u, v)) \left[\frac{\partial y}{\partial u} du + \frac{\partial y}{\partial v} dv \right] \right\}$$

$$= \int_{u_0, v_0}^{u, v} \left\{ \left[P(\phi(u, v), \psi(u, v)) \frac{\partial x}{\partial u} + Q(\phi(u, v), \psi(u, v)) \frac{\partial y}{\partial u} \right] du \right.$$

$$\left. + \left[P(\phi(u, v), \psi(u, v)) \frac{\partial x}{\partial v} + Q(\phi(u, v), \psi(u, v)) \frac{\partial y}{\partial v} \right] dv \right\}$$

$$= \int_{u_0, v_0}^{u, v} \{ \Phi(u, v) du + \Psi(u, v) dv \} , \qquad \text{(I-B-25)}$$

where Φ is set equal to

$$\left[P(\phi(u, v), \psi(u, v)) \frac{\partial x}{\partial u} + Q(\phi(u, v), \psi(u, v)) \frac{\partial y}{\partial u} \right]$$

and Q is set equal to

$$\left[P(\phi(u,v),\psi(u,v))\frac{\partial x}{\partial v}+Q(\phi(u,v),\psi(u,v))\frac{\partial y}{\partial v}\right] .$$

In order to evaluate P and Q as functions of u and v we next solve the equations

$$\Theta = P\frac{\partial x}{\partial u} + Q\frac{\partial y}{\partial u} \qquad \text{(I-B-26)}$$

and

$$\Omega = P\frac{\partial x}{\partial v} + Q\frac{\partial y}{\partial v} \qquad \text{(I-B-27)}$$

for P and Q. Thus we have

$$Q\frac{\partial y}{\partial u} = \Theta - P\frac{\partial x}{\partial u} \qquad \text{(I-B-28)}$$

and

$$Q\frac{\partial y}{\partial v} = \Omega - P\frac{\partial x}{\partial v} . \qquad \text{(I-B-29)}$$

Dividing both sides of equation (I-B-28) by $\frac{\partial y}{\partial u}$ and both sides of equation (I-B-29) by $\frac{\partial y}{\partial v}$ we obtain

$$Q = \Theta\Big/\frac{\partial y}{\partial u} - P\,\frac{\partial x}{\partial u}\Big/\frac{\partial y}{\partial u} \qquad \text{(I-B-30)}$$

and

$$Q = \Omega\Big/\frac{\partial y}{\partial v} - P\,\frac{\partial x}{\partial v}\Big/\frac{\partial y}{\partial v} \qquad \text{(I-B-31)}$$

and consequently

$$\Theta\Big/\frac{\partial y}{\partial u} - P\,\frac{\partial x}{\partial u}\Big/\frac{\partial y}{\partial u} = \Omega\Big/\frac{\partial y}{\partial v} - P\,\frac{\partial x}{\partial v}\Big/\frac{\partial y}{\partial v}\ . \qquad \text{(I-B-32)}$$

From equation (I-B-32) it follows that

$$P\,\frac{\partial x}{\partial u}\Big/\frac{\partial y}{\partial u} - P\,\frac{\partial x}{\partial v}\Big/\frac{\partial y}{\partial v} = \Theta\Big/\frac{\partial y}{\partial u} - \Omega\Big/\frac{\partial y}{\partial v}\ . \qquad \text{(I-B-33)}$$

Thus from equation (I-B-33) we obtain the value of P as a function of u and v:

$$P = \frac{\Theta\Big/\dfrac{\partial y}{\partial u} - \Omega\Big/\dfrac{\partial y}{\partial v}}{\dfrac{\partial x}{\partial u}\Big/\dfrac{\partial y}{\partial u} - \dfrac{\partial x}{\partial v}\Big/\dfrac{\partial y}{\partial v}} \qquad \text{(I-B-34)}$$

and multiplying both numerator and denominator of the right side of equation (I-B-34) by $\left(\frac{\partial y}{\partial u}\frac{\partial y}{\partial v}\right)$ we have

$$P = \frac{\Theta\dfrac{\partial y}{\partial v} - \Omega\dfrac{\partial y}{\partial u}}{\dfrac{\partial x}{\partial u}\dfrac{\partial y}{\partial v} - \dfrac{\partial x}{\partial v}\dfrac{\partial y}{\partial u}}\ . \qquad \text{(I-B-35)}$$

Now $P(x, y)$ is the total derivative of T along a line parallel to the x-axis in the (x, y)-plane.[4] Also $\Theta(u, v)$ is the total

[4] Cf. **G. Tunell**, Jour. Chem. Physics, 9, 191-192, 1941.

derivative of *T* along a line parallel to the u-axis in the (Uf v)-plane and $Q(u, v)$ is the total derivative of *T* along a line parallel to the v-axis in the (u, v)-piane. Thus from equation (I-B-35) we have

$$P(x, y) = \left(\frac{dT}{dx}\right)_y = \frac{\begin{vmatrix} \frac{dT}{du} & \frac{dT}{dv} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} \end{vmatrix}}{\begin{vmatrix} \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} \end{vmatrix}} . \qquad \text{(I-B-36)}$$

Likewise $Q(x, y)$ is the total derivative of *T* along a line parallel to the y-axis in the (x9 y)-plane. Thus in a similar way we have

$$Q(x, y) = \left(\frac{dT}{dy}\right)_x = \frac{\begin{vmatrix} \frac{dT}{du} & \frac{dT}{dv} \\ \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} \end{vmatrix}}{\begin{vmatrix} \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} \\ \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} \end{vmatrix}} . \qquad \text{(I-B-37)}$$

The determinants forming the numerators of the fractions constituting the right sides of equations (I-B-36) and (I-B-37) are similar in form to the Jacobian determinants used in the transformation of functions of two or more variables, but F is not a function of *x* and y or of u and *v* and the derivatives in the top lines of the determinants constituting the numerators of the fractions that form the right sides of equations (I-B-36) and (I-B-37) are total derivatives, not partial derivatives.

Appendix C to Part I

Discussion of P.W. Bridgman's explanation of the derivation of the functions tabulated in his book entitled *A Condensed Collection of Thermodynamic Formulas*[1]

Bridgman explained the derivation of the functions tabulated in his book entitled *A Condensed Collection of Thermodynamic Formulas* in the following way.

> All the first derivatives are of the type $\left(\frac{\partial x_1}{\partial x_2}\right)_{x_3}$ where x_x, x_2, and X3 are any three *different* variables selected from the fundamental set (for example, p, T, *v)*. The meaning of the notation is the conventional one in thermodynamics, the subscript X3 denoting that the variable x_3 is maintained constant, and the ratio of the change of *x* to the change of *X2* calculated under these conditions. The restrictions imposed by the physical nature of the system are such that derivatives of this type have a unique meaning. The number of such first derivatives evidently depends on the number of quantities selected as fundamental. For nearly all applications 10 such variables are sufficient, and this is the number taken for these tables. ...[2]
>
> Given now 10 fundamental quantities, there are 10x9x8 = 720 first derivatives. A complete collection of thermodynamic formulas for first derivatives includes all possible relations between these 720

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[1] Harvard University Press, Cambridge, 1925.

[2] The variables selected as fundamental by Bridgman are the following: the pressure p, the temperature T, the volume v, the entropy s, the heat Q, the work *w,* the energy £, the enthalpy #, the Gibbs function *z* , and the Helmholtz function ¥.

derivatives. In general, the relations involve any four of the derivatives, for any three of the derivatives are independent of each other. (There are, of course, a large number of degenerate cases in which there are relations between fewer than four derivatives.) Now, except for the degenerate cases, the number of relations between first derivatives is the number of ways in which 4 articles can be selected from 720, or

$$\frac{720\times 719\times 718\times 717}{1\times 2\times 3\times 4} = \text{approx. } 11\times 10^9 .$$

This is the number of thermodynamic relations which should be tabulated in a complete set of formulas, but such a programme is absolutely out of the question. We can, however, make it possible to obtain at once any one of the 11×10^9 relations if we merely tabulate every one of the 720 derivatives in terms of the same set of three. For to obtain the relation between any four derivatives, having expressed them in terms of the same fundamental three, we have only to eliminate the fundamental three between the four equations, leaving a single equation connecting the desired four derivatives.

This programme involves the tabulating of 720 derivatives, and is not of impossible proportions. But this number may be much further reduced by mathematical artifice. The 720 derivatives fall into 10 groups, all the derivatives of a group having the same variable held constant during the differentiation. Now each of the 72 derivatives in a group may be completely expressed in terms of only 9 quantities. Consider for example the first group, in which x_1 is the variable kept constant. Then any derivative of this group $\left(\frac{\partial x_r}{\partial x_k}\right)_{x_1}$ may be written in the form $\left(\frac{\partial x_l}{\partial x_k}\right)_{x_1} = \left(\frac{\partial x_l}{\partial \alpha}\right)_{x_1} \Big/ \left(\frac{\partial x_k}{\partial \alpha}\right)_{x_1}$, where α is any new variable, not necessarily one of the 10. Let us make this transformation for all the derivatives of the group, keeping the same α in all the transformations. Then it is evident that all derivatives of the group may be expressed in terms of the nine derivatives $\left(\frac{\partial x_2}{\partial \alpha}\right)_{x_1} \cdots \left(\frac{\partial x_{10}}{\partial \alpha}\right)_{x_1}$. By taking the ratio of the appropriate pair. That is, for the purpose of calculating the derivatives we may replace the derivative $\left(\frac{\partial x_j}{\partial x_k}\right)_{x_1}$ by the ratio of numerator to denominator, writing

$$\left(\frac{\partial x_j}{\partial x_k}\right)_{x_1} \equiv \frac{(\partial x_j)_{x_1}}{(\partial x_k)_{x_1}}$$

and then substitute for $(\partial x_j)_{x_1}$ the finite derivative $\left(\frac{\partial x_j}{\partial \alpha_1}\right)_{x_1}$ and for $(\partial x_k)_{x_1}$, $\left(\frac{\partial x_k}{\partial \alpha_1}\right)_{x_1}$.

We may now, as a short-hand method of expression, write the equations

$$(\partial x_j)_{x_1} = \left(\frac{\partial x_j}{\partial \alpha_1}\right)_{x_1}, \text{ etc.,}$$

remembering, however, that this is not strictly an equation at all (the dimensions of the two sides of the "equation" are not the same), but that the form of expression is useful because the correct result is always obtained when the ratio of two such differentials is taken.

We may proceed in this way systematically through the remaining 9 groups of 72 derivatives, choosing a new and arbitrary α for each group. We will thus have in all 90 different expressions to tabulate. This number may now be further reduced to 45 by so choosing the α's in the successive groups that the condition $(\partial x_i)_{x_j} = -(\partial x_j)_{x_i}$ is satisfied. That such a choice is possible requires proof, for having once chosen α_1, the choice of α_2 is fixed by the requirement that $(\partial x_1)_{x_2} = -(\partial x_2)_{x_1}$, and α_3 is fixed by the requirement that $(\partial x_1)_{x_3} = -(\partial x_3)_{x_1}$, so that it is now a question whether these values of α_2 and α_3 are such that $(\partial x_2)_{x_3} = -(\partial x_3)_{x_2}$. That these conditions are compatible is an immediate consequence of the mathematical identity

$$\left(\frac{\partial x_1}{\partial x_2}\right)_{x_3} \cdot \left(\frac{\partial x_2}{\partial x_3}\right)_{x_1} \cdot \left(\frac{\partial x_3}{\partial x_1}\right)_{x_2} = -1.$$

The only degree of arbitrariness left is now in α_1, which may be chosen to make the expressions as simple as possible.

In the actual construction of the tables the a's play no part, and in fact none of them need be determined; their use has been merely to show the possibility of writing a derivative as the quotient of two finite functions, one replacing the differential numerator, and the other the differential denominator. The tables were actually deduced by writing down a sufficient number of derivatives obtained by well-known thermodynamic methods, and then splitting these derivatives by inspection into the quotient of numerator and denominator. Having once fixed the value of a single one of the differentials arbitrarily, all the others are thereby fixed. For simplicity it was decided to put $(\partial x)_p = 1$.

The choice of the fundamental three derivatives leaves much latitude. It seemed best to take three which are given directly by ordinary experiment; the three chosen are

$$\left(\frac{\partial v}{\partial T}\right)_p, \left(\frac{\partial v}{\partial p}\right)_T, \text{ and } \left[C_p = \left(\frac{\partial Q}{\partial T}\right)_p\right].$$

The problem addressed by Bridgman is that of obtaining a derivative of any one variable of the 10 variables with respect to any second variable of the 10 when any third variable of the 10 is held constant in terms of the three derivatives $\left(\frac{\partial v}{\partial T}\right)_p$, $\left(\frac{\partial v}{\partial p}\right)_T$, and C_p, and certain of the thermodynamic quantities. This is a problem of obtaining derivatives with respect to a new set of independent variables in terms of derivatives with respect to an original set of independent variables. The solution of this problem by means of Jacobians was given by Bryan[3] in his article in the *Encyclopädie der matematischen Wissenschaften* in 1903 and is well established. The functions listed by Bridgman in his table as $(3p)_v$, $(3x)_v$, $(3s)_v$, $(3E)_v$, $(3p)_s$, $(3x)_s$, $(3V)_s$, $(3E)_s$, etc., are really Jacobians, not partial derivatives with respect to hypothetical auxiliary variables ot_3, a^. In the derivation by means of Jacobians explained in the preceding pages no hypothetical auxiliary variables were involved and likewise no hypothetical unknown functions of a_1 and p, or of a_2 and T, or of ot_3 and *v*, etc., were involved. Furthermore it is really not a matter of hypothesis that $(3x_1)_{x_2} = -(dx_2)_{x_1}$. The quantity $(3x_1)_{x_2}$ is really the Jacobian $\frac{\partial(x_1, x_2)}{\partial(\tau, p)}$ and the quantity $(3x_2)_{x_1}$ is really the Jacobian $\frac{\partial(x_2, x_1)}{\partial(\tau, p)}$. The Jacobian $\frac{\partial(x_1, x_2)}{\partial(\tau, p)}$ is equal to the negative of the Jacobian $\frac{\partial(x_2, x_1)}{\partial(\tau, p)}$ because interchanging two rows of a determinant changes the sign of the determinant. Finally it is not an arbitrarily adopted convention that $(3\tau)_p = 1$. The quantity $(3\tau)_p$ is equal to the Jacobian $\frac{\partial(\tau, p)}{\partial(\tau, p)}$ which is automatically equal to 1.

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[3] Bryan, G.H., in *Encyclopädie der matematischen Wissenschaften*, B.G. Teubner, Leipzig, Bd. V, Teil 1, S. 113, 1903.

Part II

Relations between thermodynamic quantities and their first derivatives in a one-component system of one phase and of variable mass

Introduction

Thermodynamic relations in open systems of one component and of one phase and other open systems have been analyzed by Gillespie and Coe,[1] Van Wylen,[2] Hall and Ibele,[3] and Beattie and Oppenheim,[4] also in part incorrectly by Larmor,[5] Morey,[6] Goranson,[7] Sage,[8] Moelwyn-Hughes,[9] Callen,[10] and Wheeler.[11]

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[1] Gillespie, L.J., and J.R. Coe, Jr., Jour. Chem. Phys., 1, 103-113, 1933.

[2] Van Wylen, G.J., *Thermodynamics,* John Wiley and Sons, Inc., New York, Chapman and Hall, London, 1959.

[3] Hall, N.A., and W.E. Ibele, *Engineering Thermodynamics,* Prentice-Hall, Inc., Englewood-Cliffs, N.J., 1960.

** Beattie, J.A., and Irwin Oppenheim, *Principles of Thermodynamics,* Elsevier Scientific Publishing Co., Amsterdam, Oxford, New York, 1979, pp. 296-320.

[5] Larmor, Sir Joseph, Proc. Roy. Soc. London, 75, 280-296, 1905.

[5] Morey, G.W., Jour. Franklin Inst., 194, 425-484, 1922.

[7] Goranson, R.W., *Thermodynamic Relations in Multi-Component Systems,* Carnegie Institution of Washington Publication No. 408, 1930.

[8] Sage, B.H., *Thermodynamics of Multicomponent Systems,* Reinhold Publishing Corp., New York, 1965.

[9] Moelwyn-Hughes, E.A., *Physical Chemistry,* Pergamon Press, London, New York, Paris, 1957.

[10] Callen, H.E., *Thermodynamics,* John Wiley and Sons, Inc., New York and London, 1960.

[11] Wheeler, L.P., *Josiah Willard Gibbs - The History of a Great Mind,* Rev. Ed., Yale University Press, Mew Haven, 1952,

In the following text the relations for the energy and the entropy of a one-component system of one phase and of variable mass are derived and a table of Jacobians is presented by means of which any first partial derivative of any one of the quantities, the absolute thermodynamic temperature T, the pressure p, the total mass M_f the total volume V, the total energy U, and the total entropy 5, with respect to any other of these quantities can be obtained in terms of the partial derivative of the specific volume with respect to the temperature, the partial derivative of the specific volume with respect to the pressure, the heat capacity at constant pressure per unit of mass, and certain of the quantities 7\ p, Aft V, U, S.

In the case of a one-component system of one phase and of variable mass it is not necessary to make use of a definition of heat or a definition of work in the case of an open system when mass is being transferred to or from the system in order to derive the relations for the total energy and the total entropy. For some purposes, however, it has been found useful to have definitions of heat and work in the case of open systems when mass is being transferred to or from the system. The definitions of heat and work in the case of open systems used by various authors are discussed in Appendix A to Part II.

Calculation of the total volume, the total energy, and the total entropy of a one-component system of one phase and of variable mass as functions of the absolute thermodynamic temperature, the pressure, and the total mass

Thermodynamic formulas can be developed in the case of a one-component system of one phase and of variable mass on the basis of the following set of variable quantities: the absolute thermodynamic temperature T_t the pressure P, the

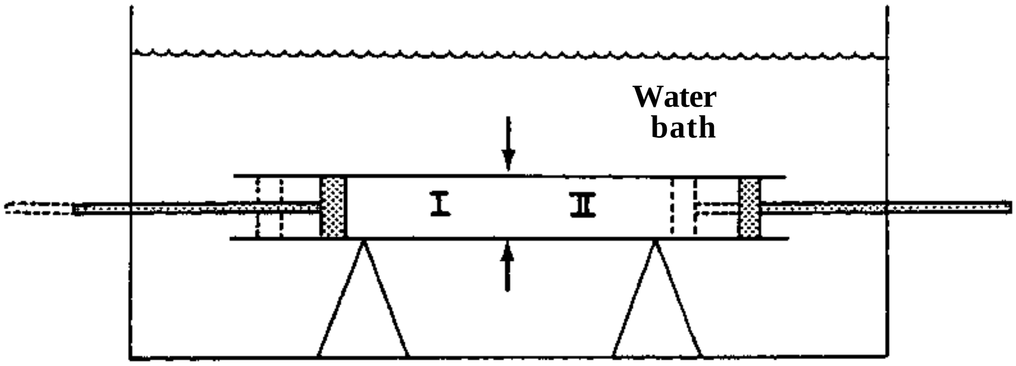

Figure II-1

total mass *M,* the total volume *V,* the total energy *U*, the total entropy 5, the specific volume *V,* the specific energy *U,* the specific entropy 5, the heat capacity at constant pressure per unit of mass $\breve{c}_p$, and the latent heat of change of pressure at constant temperature per unit of mass l_p. Two one-component systems of one phase and of variable mass are illustrated in Figure II–1• The formulas developed in the following pages apply to either open system I or open system II in Figure II–1. Open systems I and II together constitute a closed system.

In the case of a one-component system of one phase and of variable mass the total volume *V* is a function of the absolute thermodynamic temperature *T,* the pressure p, and the total mass *M*

$$V = f(7, p, M) \ . \tag{II-l}$$

The total volume is equal to the total mass times the specific vo1ume

$$V = M\breve{V} \ , \tag{H-2}$$

and the specific volume is a function of the absolute thermodynamic temperature and the pressure,

$$V = <t>(T, p) \ . \tag{II-3}$$

From equations (II-l), (II-2), and (II-3) it follows that

$$\left(\frac{\partial V}{[illegible]}\right)_{T,p} [illegible] \Big)_{T,p} \ . \tag{II-4}$$

$$\left(\frac{\partial V}{\partial p}\right)_{T,\,M} = M\left(\frac{\partial \breve{V}}{\partial p}\right)_{T} , \qquad \text{(II-5)}$$

and

$$\left(\frac{\partial V}{\partial M}\right)_{T,\,p} = \breve{V} . \qquad \text{(II-6)}$$

The total energy is a function of the absolute thermodynamic temperature, the pressure, and the total mass

$$U = MT, p, M) . \qquad \text{(H-7)}$$

It is known that the total energy of a one-component system of one phase and of variable mass is proportional to the total mass at a given temperature and a given pressure because it requires *M* times as much heat received and *M* times as much work done to take *M* times as much substance from the standard state to the given state as to take unit mass of the substance from the standard state to the given state through the same set of intermediate states. Thus the total energy is equal to the total mass times the specific energy

$$U = M\breve{U} . \qquad \text{(II-8)}$$

Furthermore it is known from the case of a one-component system of one phase and of unit mass discussed in part I that the specific energy is a function of the absolute thermodynamic temperature and the pressure

$$\breve{U} = 8(T, p) . \qquad \text{(H-9)}$$

Thus the relation of the total energy to the absolute thermodynamic temperature, the pressure, and the total mass is expressed by the equation

$$U(T, p, M) - U(T_0, p_0, M_0)$$

$$= \int_{T_0,\, p_0,\, M_0} \left\{ M\left[\breve{c}_p - p\frac{\partial \breve{V}}{\partial T}\right]dT + M\left[\breve{l}_p - p\frac{\partial \breve{V}}{\partial p}\right]dp + \breve{U}dM \right\}. \qquad \text{(II-10)}$$

From equations (II-7), (II-8), (II-9), and (II-10) it follows that

$$\left(\frac{\partial U}{\partial T}\right)_{p,\, M} = M\left[\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right] , \qquad \text{(II-11)}$$

$$\left(\frac{\partial U}{\partial p}\right)_{T,\, M} = M\left[\breve{l}_p - p\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right] , \qquad \text{(II-12)}$$

and

$$\left(\frac{\partial U}{\partial M}\right)_{T,\, p} = \breve{U} . \qquad \text{(II-13)}$$

The total entropy is a function of the absolute thermodynamic temperature, the pressure, and the total mass

$$S = S(T, p, M) . \qquad \text{(II-14)}$$

It is known that the total entropy of a one-component system of one phase and of variable mass is proportional to the total mass at a given temperature and a given pressure because it requires M times as much heat received to take M times as much substance from the standard state to the given state as to take unit mass of the substance from the standard state to the given state reversibly through the same set of intermediate states. Thus the total entropy is equal to the total mass times the specific entropy

$$S = M\breve{S} . \qquad (11\text{-}15)$$

Furthermore it is known from the case of a one-component system of one phase and of unit mass discussed in Part I that the specific entropy is a function of the absolute thermodynamic temperature and the pressure

$$\breve{S} = \varphi(T, p) . \qquad (11\text{-}16)$$

Thus the relation of the total entropy to the absolute thermodynamic temperature, the pressure, and the total mass is expressed by the equation

$$S(T, p, M) - S(T_0, p_0, M_0)$$

$$= \int_{T_0, p_0, M_0}^{T, p, M} \left\{ M\frac{\breve{c}_p}{T}dT + M\breve{f}\,dp + \breve{S}dM \right\} . \qquad (11\text{-}17)$$

From equations (11-14), (11-15), (11-16), and (11-17) it

follows that

$$\left(\frac{\partial S}{\partial T}\right)_{p,\,M} = M\frac{\breve{c}_p}{T}, \qquad \text{(II-18)}$$

$$\left(\frac{\partial S}{\partial p}\right)_{T,\,M} = M\frac{\breve{l}_p}{T}, \qquad \text{(II-19)}$$

and

$$\left(\frac{\partial S}{\partial M}\right)_{T,\,p} = [illegible] \qquad \text{(II-20)}$$

It is to be noted that the derivations of equations (11-10) and (11-17) do not depend on definitions of heat and work in the case of open systems.[12] In equation (11-10) the coefficient of *dT* is the partial derivative of the total energy with respect to temperature at constant pressure and constant mass, which is known from the case of a one-component one-phase closed system to be $M\left[\breve{c}_p - p\frac{\partial \breve{v}}{\partial T}\right]$. Likewise the coefficient of *dp* in equation (11-10) is the partial derivative of the total energy with respect to pressure at constant temperature and constant mass, which is known from the case of a one-component one-phase closed system to be $M\left[\breve{l}_p - p\frac{\partial \breve{v}}{\partial p}\right]$. The coefficient of *dM* in equation (11-10) is

[12] It is possible to define heat and work in the case of a one-component system of one phase and of variable mass and this has been found to have usefulness in some engineering problems. See Appendix A to Part II.

the partial derivative of the total energy with respect to mass, which is simply the specific energy, because the addition of mass is at constant temperature and constant pressure. Likewise in equation (11-17) the coefficient of dT is the partial derivative of the total entropy with respect to temperature at constant pressure and constant mass, which is known from the case of a one-component one-phase closed system to be $M\frac{\breve{c}_p}{T}$. Also in equation (11-17) the coefficient of dp is the partial derivative of the total entropy with respect to pressure at constant temperature and constant mass, which is known from the case of a one-component one-phase closed system to be $M\frac{\breve{l}_p}{T}$. The coefficient of dM in equation (11-17) is the partial derivative of the total entropy with respect to mass, which is simply the specific entropy, because the addition of mass is at constant temperature and constant pressure.

Necessary and sufficient conditions for (11-10) to be true are

$$\left\{\frac{\partial\left[M\left(\breve{l}_p - p\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right)\right]}{\partial T}\right\}_{p,M} = \left\{\frac{\partial\left[M\left(\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right)\right]}{\partial p}\right\}_{T,M}, \quad \text{(II-21)}$$

$$\left(\frac{\partial U}{\partial T}\right)_{p,M} = \left\{\frac{\partial\left[\text{r*\\ML} \sim M)\right)_p\right]}{\partial M}\right\} . \quad \text{(n-22)}$$

and

$$\left(\frac{\partial U}{\partial p}\right)_{T,M} = \left\{\frac{\partial\left[M\left(\breve{l}_p - p\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right)\right]}{\partial M}\right\}_{T,p} . \quad [13] \qquad \text{(II-23)}$$

Similarly, necessary and sufficient conditions for (11-17) to be true are

$$\left(\frac{\partial\left(M\frac{\breve{l}_p}{T}\right)}{\partial T}\right)_{p,M} = \left(\frac{\partial\left(M\frac{\breve{c}_p}{T}\right)}{\partial p}\right)_{T,M} , \qquad \text{(II-24)}$$

$$\left(\frac{\partial\ }{\partial T}\right)_{p,M} = \left(\frac{\partial\left(M\frac{\breve{c}_p}{T}\right)}{\partial M}\right)_{T,p} . \qquad \text{(II-25)}$$

and

$$\left(\frac{\partial S}{\partial p}\right)_{T,M} = \left(\frac{\partial\left(M\frac{\breve{l}_p}{T}\right)}{\partial M}\right)_{T,p} . \qquad \text{(II-26)}$$

Carrying out the indicated differentiations in (11-21) and

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[13] Osgood, W.F., *Advanced Calculus*, The Macoillan Co., New York, 1925, p. 232, and Osgood, W.F., *Lehrbuch der Funktionentheorie*, B.G. Teubner, Leipzig, 5te Aufl., 1928, Bd. I, S. 142-150.

(11-24) one obtains

$$M \frac{p}{\partial T} \quad .. \quad 9F \quad M 3 \breve{c}_p \quad 8y \quad 3F \qquad ,TT\ 97,$$

and

$$M \frac{1}{T} \frac{\partial \breve{l}_p}{\partial T} - M \frac{\breve{l}_p}{T^2} = M \frac{1}{T} \frac{\partial \breve{c}_p}{\partial p} \, . \qquad \text{(II-28)}$$

Combining (11-27) and (11-28) one has

$$h = -r|£ \, . \qquad \text{(ii-29)}$$

From (11-27) and (11-29) it also follows that

$$\wedge_{\partial p} = -r|S_{\partial T} \quad * \qquad \text{(II-30)}$$

From (11-22), (11-23), (11-25), and (11-26) only the already known equations

$$\frac{d\breve{U}}{df} = \tilde{\circ P} - p \frac{\partial \breve{V}}{\partial T} \, , \qquad \text{(II-31)}$$

$$\partial \breve{U} \quad \breve{j} \quad \partial \breve{V} \qquad /TT\ on\backslash$$

$$|\breve{f} = \breve{\wedge} \quad ' \qquad \text{(II-33)}$$

and

$$I = \frac{\breve{l}_p}{T} \,, \qquad \text{(II-34)}$$

are derived,

Thus in order to obtain complete thermodynamic information for a one-component system of one phase and of variable mass it is only necessary to determine experimentally the specific volume as a function of temperature and pressure and the heat capacity at constant pressure per unit of mass as a function of temperature at one pressure. This is the same conclusion as the one reached by Bridgman[14] in the case of a one-component system of one phase and of constant mass. No additional measurements are required to obtain complete thermodynamic information for a one-component system of one phase and of variable mass beyond those required to obtain complete thermodynamic information for a one-component system of one phase and of constant mass.

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[14] Bricigroan, P.M., Phys. Rev., (2), 3, 274, 1914.

Derivation of any desired relation between the thermodynamic quantities T, p, M, V, U, S and their first derivatives for a one-component system of one phase and of variable mass by the use of functional determinants (Jacobians)

Equations (II-1), (II-10) and (II-17) can, in general, be solved for any three of the quantities, T, p, M, V, U, S, as functions of the remaining three. The first partial derivative of any one of the quantities, T, p, M, V, U, S with respect to any second quantity when any third and fourth quantities are held constant can be obtained in terms of the three first derivatives, $\left(\frac{\partial V}{\partial T}\right)_p$, $\left(\frac{\partial V}{\partial p}\right)_T$ and C_p, and certain of the quantities, T, p, M, V, U, S by application of the theorem[15] stating that, if $x' = \psi(x, y, z)$, $x = f(u, v, w)$, $y = \phi(u, v, w)$, $z = \psi(u, v, w)$, then one has

$$\left(\frac{\partial x'}{\partial x}\right)_{y,z} = \frac{\begin{vmatrix} \frac{\partial x'}{\partial u} & \frac{\partial x'}{\partial v} & \frac{\partial x'}{\partial w} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \\ \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \end{vmatrix}}{\begin{vmatrix} \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} & \frac{\partial x}{\partial w} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \\ \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \end{vmatrix}} = \frac{\dfrac{\partial(x', y, z)}{\partial(u, v, w)}}{\dfrac{\partial(x, y, z)}{\partial(u, v, w)}}, \qquad \text{(II-35)}$$

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[15] A proof of this theorem for the case of functions of three independent variables is given in Appendix C to Part II.

provided all the partial derivatives in the determinants are continuous and provided the determinant in the denominator is not equal to zero.

In Tables II-1 to 11-15 the values of the Jacobians are given for each set of three of the variables, T, p, M, V, U, S, as x, y, z, or x, y, z, and with T, p, M, as u, v, w. There are sixty Jacobians in the Table, but one has

$$\frac{\partial(x, y, z)}{\partial(u, v, w)} = -\frac{\partial(z, y, x)}{\partial(u, v, w)} = \frac{\partial(y, z, x)}{\partial(u, v, w)} \qquad (11\text{-}36),\ (11\text{-}37)$$

because interchanging two rows of a determinant changes the sign of the determinant. Hence it is only necessary to calculate the values of twenty of the sixty Jacobians. The calculations of these twenty Jacobians follow:

$$\frac{\partial(M, T, p)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial M} \end{vmatrix} = 1 ; \qquad (11\text{-}38)$$

$$\frac{\partial(V, T, p)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial M} \end{vmatrix} = \left(\frac{\partial V}{\partial M}\right)_{T,p} = \breve{V} ; \qquad (11\text{-}39)$$

$$\frac{\partial(U, T, p)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial M} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial M} \end{vmatrix} = \left(\frac{\partial U}{\partial M}\right)_{T, p} = \breve{U}; \tag{11-40}$$

$$\frac{\partial(S, T, p)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial M} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial M} \end{vmatrix} = \left(\frac{\partial S}{\partial M}\right)_{T, p} = \breve{S}; \tag{11-41}$$

$$\frac{\partial(V, T, M)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \end{vmatrix} = -M\left(\frac{\partial \breve{V}}{\partial p}\right)_{T}; \tag{11-42}$$

$$\frac{\partial(U, T, M)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial M} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \end{vmatrix} = M\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p} + p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T}\right] \cdots \tag{11-43}$$

$$\frac{\partial(S,T,M)}{\partial(T,p,M)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial M} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \end{vmatrix} = M\left(\frac{\partial \breve{V}}{\partial T}\right)_p ; \qquad \text{(II-44)}$$

$$\frac{\partial(U,T,V)}{\partial(T,p,M)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial M} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \end{vmatrix} = M\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{V}}{\partial p}\right)_T + \breve{V}T\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right] ; \qquad \text{(II-45)}$$

$$\frac{\partial(S,T,V)}{\partial(T,p,M)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial M} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \end{vmatrix} = M\left[\breve{V}\left(\frac{\partial \breve{V}}{\partial T}\right)_p + \breve{S}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right] ; \qquad \text{(II-46)}$$

$$\frac{\partial(S,T,U)}{\partial(T,p,M)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial M} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial M} \end{vmatrix} = M\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial T}\right)_p - \breve{S}p\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right] ; \qquad \text{(II-47)}$$

$$\frac{\partial(V, p, M)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial M} \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \end{vmatrix} = M\left(\frac{\partial \breve{V}}{\partial T}\right)_p \; ; \tag{11-48}$$

$$\frac{\partial(U, p, M)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial M} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial M} \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \end{vmatrix} = M\left[\breve{C}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right] \; ; \tag{11-49}$$

$$\frac{\partial(S, p, M)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial M} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial M} \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \end{vmatrix} = M\,\frac{\breve{C}_p}{T} \; ; \tag{11-50}$$

$$\frac{\partial(U, p, V)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial M} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial M} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \end{vmatrix} = -M\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{V}}{\partial T}\right)_p - \breve{C}_p\breve{V}\right] \; ; \tag{11-51}$$

$$\frac{\partial(S,p,V)}{\partial(T,p,M)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial M} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial M} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \end{vmatrix} = M\left[\frac{\breve{c}_p}{T}\breve{V} - \breve{S}\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]; \qquad (11\text{-}52)$$

$$\frac{\partial(S,p,U)}{\partial(T,p,M)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial M} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial M} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial M} \end{vmatrix} = M\left[\frac{\breve{c}_p}{T}(\breve{U} - T\breve{S}) + \breve{S}p\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]; \qquad (11\text{-}53)$$

$$\frac{\partial(U,M,V)}{\partial(T,p,M)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial M} \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \end{vmatrix} = -M^2\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)_p + \breve{c}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]; \qquad (11\text{-}54)$$

$$\frac{\partial(S,M,V)}{\partial(T,p,M)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial M} \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \end{vmatrix} = -M^2\left[\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]; \qquad (11\text{-}55)$$

$$\frac{\partial(S, M, U)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial M} \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial M} \end{vmatrix} = M^2\left[p\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{p\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right] ; \tag{11-56}$$

$$\frac{\partial(S, V, U)}{\partial(T, p, M)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial M} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial M} \end{vmatrix}$$

$$= M^2\left\{\left[\breve{U} + p\breve{V} - T\breve{S}\right]\left[\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]\right\} . \tag{11-57}$$

Table II-1
Jacobians of extensive functions for a one-component system of one phase

$$\frac{\partial(x', y, z)}{\partial(T, p, M)} \quad , \quad \frac{\partial(x, y, z)}{\partial(T, p, n)}$$

x \ y, z	T, p
M	1
V	$\breve{V}$
U	V
S	$\breve{S}$

Table II-2
Jacobians of extensive functions for a one-component system of one phase

$$\frac{\partial(x', y, z)}{\partial(T, p, M)}, \quad \frac{\partial(x, y, z)}{\partial(T, p, M)}$$

x \ y, z	T, M
P	-1
V	$-M\left(\frac{\partial \breve{V}}{\partial p}\right)_T$
U	« [r ©p * ' (111
S	$M\left(\frac{\partial \breve{V}}{\partial T}\right)_p$

Table II-3
Jacobians of extensive functions for a
one-component system of one phase

$$\frac{\partial(x', y, z)}{\partial(T, p, M)} = \frac{\partial(x, y, z)}{\partial(T, p, M)}$$

x' \ y, z	T, V
p	$-\breve{V}$
M	$M\left(\frac{\partial \breve{V}}{\partial p}\right)_T$
U	$M\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{V}}{\partial p}\right)_T + \breve{V}T\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]$
S	$M\left[\breve{V}\left(\frac{\partial \breve{V}}{\partial T}\right)_p + \breve{S}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$

Table II-4
Jacobians of extensive functions for a
one-component system of one phase

$$\frac{\partial(W, y, z)}{\partial(T, p, M)} = \frac{\partial(x, y, z)}{\partial(T, p, M)}$$

$x \backslash y, z$	T, U
p	$-\breve{U}$
M	$-M\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)_p + p\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$
V	$-M\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{V}}{\partial p}\right)_T + \breve{V}T\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]$
S	$M\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial T}\right)_p - \breve{S}p\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$

Table II-5
Jacobians of extensive functions for a one-component system of one phase

$$\frac{\partial(x', y, z)}{\partial(T,p,M)}, \quad \frac{\partial(x, y, z)}{\partial(T,p,M)}$$

x' \ x	T, S
p	$-S$
M	$\cdot \gg (i)_p$
V	$-M\left[\breve{V}\left(\frac{\partial \breve{V}}{\partial T}\right)_p + \breve{S}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$
U	$-M\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial T}\right)_p - \breve{S}p\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$

Table II-6
Jacobians of extensive functions for a one-component system of one phase

$$\frac{\partial(x, y, z)}{\partial(T,p,M)}, \quad \frac{\partial(x, y, z)}{\partial(T,p,M)}$$

x \	p, M
T	1
V	$M\left(\frac{\partial \breve{V}}{\partial T}\right)_p$
U	$M\left[\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]$
S	$M\frac{\breve{c}_p}{T}$

Table II-7
Jacobians of extensive functions for a one-component system of one phase

d(x', Yf z) / d(T,p,M) ' 3(x, y, z) / 3(T, p,M)

\Yt Z x'\ X	P;V
T	V
M	$-M\left(\frac{\partial V}{\partial T}\right)_p$
u	-M[CU * p?)(ff)p - ? /]
S	-[?» - S1Ï)J

Table II-8
Jacobians of extensive functions for a one-component system of one phase

$$\frac{\partial(x', y, z)}{\partial(T, p, M)}, \frac{\partial(x, y, z)}{\partial(T, p, M)}$$

y, z / x	$p, \breve{U}$
T	$\breve{U}$
M	$-M\left[\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]$
V	$M\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{V}}{\partial T}\right)_p - \breve{c}_p\breve{V}\right]$
S	$M\left[\frac{\breve{c}_p}{T}(\breve{U} - T\breve{S}) + \breve{S}p\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]$

Table II-9
Jacobians of extensive functions for a
one-component system of one phase

d(x', v, z) / KT,p,M) f 3(x, v, z) / 3(T, p,Af)

y, z / x', x	p,S
T	*»/ S
H	$-M \frac{\breve{C}_p}{T}$
y	Λ[>* - =(f)J
U	$-M\left[\frac{\breve{C}_p}{T}(\breve{U} - T\breve{S}) + \breve{S}p\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]$

Table 11-10
Jacobians of extensive functions for a
one-component system of one phase

$$\frac{\partial(x, y, z)}{\partial(T, p, M)}, \quad \frac{\partial(x', y, z)}{\partial(T, p, M)}$$

y, z / x', x	M, V
T	$-M\left(\frac{\partial \breve{V}}{\partial p}\right)_T$
p	$M\left(\frac{\partial \breve{V}}{\partial T}\right)_p$
U	$-M^2\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \breve{c}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$
S	$-M^2\left[\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$

Table 11-11
Jacobians of extensive functions for a
one-component system of one phase

$$\frac{\partial(x, y, z)}{\partial(T, p, M)} * \frac{\partial(x, y, z)}{\partial(T_f\, p, M)}$$

\y» z * ' \ x X	A/, (/
T	4#)/'(l)J
P	$M\left[\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]$
V	$M^2\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \breve{c}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$
S	$M^2\left[p\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{p\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$

Table 11-12
Jacobians of extensive functions for a
one-component system of one phase

$$\frac{d(x', v, z)}{d\{T,p,M)}\ ',\quad \frac{a(x, y, z)}{3(T, p,M)}$$

x' \ x	M, S
T	JdV̆\
P	$M\frac{\breve{c}_p}{T}$
V	$M^2\left[\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$
U	$-M^2\left[p\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{p\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$

Table 11-13
Jacobians of extensive functions for a one-component system of one phase

$$\frac{\partial(x', y, z)}{\partial(T, p, M)} ; \frac{\partial(x, y, z)}{\partial(T, p, M)}$$

x' \ y, z x	T, U
T	$M\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{V}}{\partial p}\right)_T + \breve{V}T\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]$
p	$-M\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{V}}{\partial T}\right)_p - \breve{c}_p\breve{V}\right]$
X	$-M^2\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \breve{c}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$
S	$M^2\left\{\left[\breve{U} + p\breve{V} - T\breve{S}\right]\left[\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]\right\}$

Table 11-14
Jacobians of extensive functions for a one-component system of one phase

$$\frac{\partial(x, y, z)}{\partial(T, p, N)} = \frac{\partial(x, y, z)}{\partial(T, p, N)}$$

x \ y, z	V, S
T	f(ĭ)/²(li]
p	$N\left[\frac{\breve{C}_p}{T}\breve{V} - \breve{S}\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]$
N	-[(H²)/*(li]
U	$-N^2\left\{\left[\breve{U} + p\breve{V} - T\breve{S}\right]\left[\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]\right\}$

Table 11-15
Jacobians of extensive functions for a one-component system of one phase

$$\frac{\partial(x', y, z)}{\partial(T, p, M)} \div \frac{\partial(x, y, z)}{\partial(T, p, M)}$$

x' \ y, z x	U, S
T	$M\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial T}\right)_p - \breve{S}p\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$
P	$M\left[\frac{\breve{C}_p}{T}(\breve{U} - T\breve{S}) + \breve{S}p\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right]$
M	$M^2\left[p\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{p\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]$
U	$M^2\left\{\left[\breve{U} + p\breve{V} - T\breve{S}\right]\left[\left(\frac{\partial \breve{V}}{\partial T}\right)_p^2 + \frac{\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right]\right\}$

In order to obtain the first partial derivative of any-one of the six quantities, T, p, M, V, U, S, with respect to any second quantity of the six when any third and fourth quantities of the six are held constant, one has only to divide the value of the Jacobian in which the first letter in the first line is the quantity being differentiated and in which the second and third letters in the first line are the quantities held constant by the value of the Jacobian in which the first letter of the first line is the quantity with respect to which the differentiation is taking place and in which the second and third letters in the first line are the quantities held constant.

To obtain the relation among any four derivatives having expressed them in terms of the same three derivatives, $\left(\frac{\partial V}{\partial T}\right)_p$, $\left(\frac{\partial V}{\partial p}\right)_T$, and C_p, one can then eliminate the three derivatives from the four equations, leaving a single equation connecting the four derivatives. In addition to the relations among four derivatives there are also degenerate cases in which there are relations among fewer than four derivatives.

In case a relation is needed that involves one or more of the thermodynamic potential functions, $H \equiv U + pV$, $A \equiv U - TS$, $G \equiv U + pV - TS$, partial derivatives involving one or more of these functions can also be calculated as the quotients of two Jacobians, which can themselves be calculated by the same method used to calculate the Jacobians in Tables II-1 to II-15.

It is interesting to note that in the transformations of the thermodynamic quantities T, p, M, V, U, S from one coordinate space based on any three of these six quantities to another coordinate space likewise based on three of these six quantities, the enthalpy H, the Helmholtz function A, and the Gibbs function G appear automatically in the expressions for many of the Jacobians involved.

Appendix A to Part II

Discussion of the definitions of heat and work in the case of open systems used by various authors

According to Larmor,[1] Morey,[2] Goranson,[3] Moelwyn-Hughes, ** Callen,[5] and Wheeler[6] in the case of an open system to which mass is added or from which mass is taken away, the differential of the heat received *dQ* is equal to the absolute thermodynamic temperature *T* times the differential of the entropy of the system *dS.* Neither Larmor nor Morey nor Goranson nor Moelwyn-Hughes nor Callen gave an operational analysis of any open system in support of their conclusion that *dQ* = *TdS* in the case of open systems. Wheeler attempted to explain the Gibbs differential equation for an open system

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[1] Larmor, Sir Joseph, Proc. Roy. Soc. London, 75, 289-290, 1905.

[2] Morey, G.W., Jour. Franklin Inst., 194, 433-434, 1922.

[3] Goranson, R.W., *Thermodynamic Relations in Multi-Component Systems,* Carnegie Institution of Washington Publication No. 408, 1930, pp. 39, 41, 44, 52.

% Moelwyn-Hughes, E.A., *Physical Chemistry,* Pergamon Press, London, New York, Paris, 1957, p. 287.

[5] Callen, H.B., *Thermodynamics$* John Wiley and Sons, Inc., New York and London, 1960, p« 192.

[6] Wheeler, L.P., *Josiah Willard Gihbs-The History of a Great Mind,* Rev. Ed.f Yale University Press, Mew Haven, 1952, p. 76.

of n components

$$dU = TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2 \ldots + \mu_n dm_n$$ [7]

where $\mu_1, \mu_2, \ldots \mu_n$ denote the chemical potentials of components 1, 2, ... n, and $m_1, m_2, \ldots m_n$ denote the masses of components 1, 2, ... n in the open system, in the following way. Wheeler supposed that an:

> . . . imaginary box is constructed with walls which in addition to being elastic and thermally conducting are also porous, so that the solution can pass freely through the pores in either direction - from inside out or from outside in. Then if the condition of the fluid is slightly altered as before, the change in energy in the box will depend not only on the heat which may enter or leave and the volume change due to the buckling of the walls but also on the masses of the components of the fluid going through the pores. Thus this energy change cannot be computed by the prime equation[8] as it stands. It must be altered by the addition of as many energy terms as there are components of the fluid passing through the walls. If there are n such components, the generalized prime equation will express the change in energy in terms of *n* + 2 independent variables. Each of the added

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[7] Gibbs, J. Willard, Trans. Conn. Acad. of Arts and Sciences, 3, 116, 1874-78, or *Collected Works,* Longmans, Green and Co., New York, 1928, **Vol.** 1, p. 63.

[8] The equation here referred to as the prime equation is the Clausius differential equation for closed systems:

$$dU = TdS - pdV.$$

> energy terms, in analogy to those in the prime equation, Gibbs expresses as the product of two factors, one an intensity and the other an extension factor. Thus just as the heat term is expressed as the product of temperature and the change in entropy, and the work term as the product of pressure and the change in volume, so an energy term due to the added mass of any component was expressed as the product of what Gibbs termed a "potential" and the change in mass.

However, according to Gillespie and Coe[9] in the case of an open system

$$dS = \frac{dQ}{T} + \sum_i \breve{S}_i dm_i \qquad \text{(II-A-1)}$$

when there is simultaneous reversible transfer of both heat and mass. In this equation, *dS* denotes the increase in the entropy of the open system, *dQ* the amount of heat received by the open system, *T* the absolute thermodynamic temperature of the open system, $\breve{S}_i$ the entropy of unit mass of kind i added to the open system, and dm_i the mass of kind i added to the open system.

The equation of Gillespie and Coe applied to the case of an open system in which there is simultaneous reversible transfer of both heat and mass appears to be correct. Let us consider the following simplest imaginable case of an open system. In a thermostat filled with water, suppose that one has a cylinder closed at both ends by pistons and containing a

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[9] Gillespie, L.J., and J.E. Coe, Jr., Jour. Chem. Phys., 1, 105, 1933.

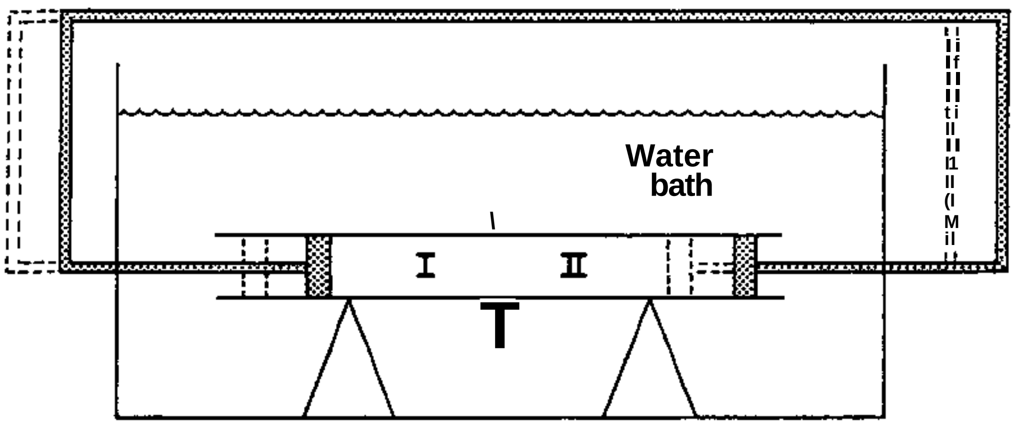

Figure II-A-1

fluid of constant composition (Figure II-A-1). Suppose further that the pistons are connected by a rigid bar so that the volume between them remains constant. In Figure II-A-1, let the two arrows indicate the position of a fixed circular line around the cylinder. The fluid between the two pistons constitutes a closed system and at this stage the temperature, pressure, and volume of the total mass of fluid are kept constant. Let us next suppose that the two pistons are moved slowly to the left in unison from the positions indicated in Figure II-A-1 by solid lines to the positions indicated by dotted lines. The mass of fluid to the left of the arrows then has received an addition and that to the right of the arrows has undergone a diminution. The mass of fluid to the left of the arrows has constituted an open system which we designate as system I. Likewise, the mass of fluid to the right of the arrows has constituted a second open system which we designate as system II. Systems I and II together make up a closed system, the entropy of which has remained constant. The entropy of system I, S^, has increased by an amount equal to the specific entropy of the fluid times the mass of the fluid that has been moved past the arrows from right to left and the entropy of system II, S-^, has decreased by the same amount. Thus, we had:

$$dS^{1} \ll \breve{S}dAf^{1}, \qquad \text{(II-A-2)}$$

$$dS^{11} \ll \breve{S}dM^{11} = -\breve{S}dM^{1}; \qquad \text{(II-A-3)(II-A-4)}$$

and

$$dS^{I} + dS^{II} = 0, \qquad \text{(II-A-5)}$$

where $\breve{S}$ denotes the specific entropy of the fluid and M^ and

A/II denote the masses of systems I and II. At the same time, no heat has been received by the fluid from the water bath since the temperature of the fluid has remained the same as that of the water bath and the pressure and total volume of the fluid have remained constant. The question then remains to be answered whether or not it can be said that system I has received any heat and similarly whether or not system II has given up any heat. To say that at constant temperature, constant pressure, and constant specific volume *x* grams of fluid have transported y calories of heat from system II to system I is the same as saying that these *x* grams of fluid at the constant temperature $t^{}$ and constant pressure p^f contained y calories of heat which they carried with them. It is well known in calorimetry, thermodynamics, and statistical mechanics that it is not possible to say that a body at a certain temperature and pressure contains a certain amount of heat* Doolittle and Zerban[10] have stated that "most modern authors of texts on thermodynamics and on physics have agreed on the following conception of heat: Heat is energy transferred from one substance to another substance because of a temperature difference between the two substances.ff In the case we have been discussing, system I, system II, and the water bath of the thermostat have all remained at the same temperature. Consequently, it cannot be said that there has been any heat flow from the water bath to system I or system II or from system II to system I. At constant temperature, constant pressure, and constant specific volume, we thus had:

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[10] Doolittle, J.S., and **A.H. Zerban,** *Engineering Thermodynamics,* International Textbook Co., Scranton, 1948, p. 8.

$$dQ^{I} = 0, \qquad \text{(II-A-6)}$$

$$dQ^{II} = 0, \qquad \text{(II-A-7)}$$

and

$$dQ^{I} + dQ^{II} = 0, \qquad \text{(II-A-8)}$$

where Q^{I} and Q^{II} denote the heat quantities received by systems I and II. Thus the heat received by a one-component system of one phase and of variable mass can be represented by the line integral

$$Q = \int^{T,p,M} \{M c_p dT + M l_p dp + 0\,dM\}\,[11] \qquad \text{(II-A-9)}$$

where c_p and l_p are functions of T and p and the coefficient of *dM* is zero.

We turn next to the question of the definition of work in the case of a one-component system of one phase and of variable mass. In this case it remains to be determined whether or not *dM* is equal to *pdV* if one wishes to introduce a definition of work in the case of an open system when mass is being transferred to or from the system. Several authors,

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[11] The question of the definition of the heat received by a one-conponent system of one phase and of variable mass has been discussed by this author more comprehensively on pages 17 to 33 of Carnegie Institution of Washington Publication No. 408A entitled *Tbermodynamic Relations in Open Systems* published in 1977.

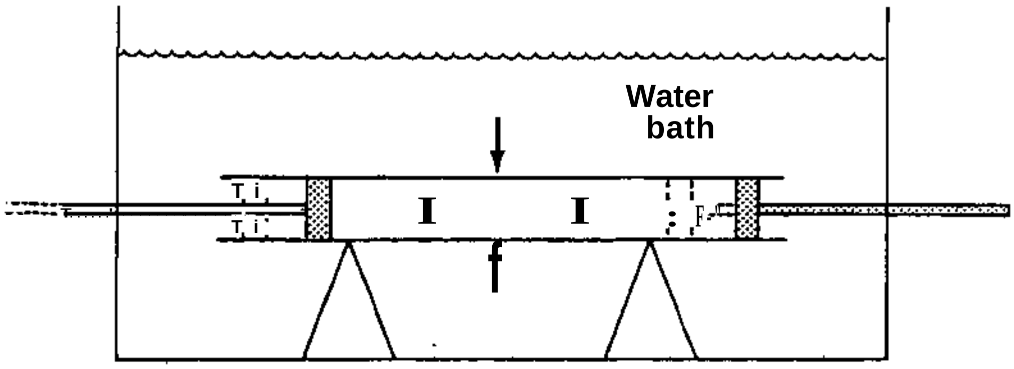

Figure II-A-2

Morey,[12] Goranson,[13] Moelwyn-Hughes,[14] and Wheeler,[15] have stated that in the GIbbs differential equation $dW = pdV$. However, none of these authors drew a diagram of an open system and none of them apparently realized that this statement does not carry over from the Clausius differential equation for a closed system without the necessity of an important new physical decision.

In regard to the question of the definition of work in the case of an open system, we may note that G.J. Van Wylen,[16] formerly Chairman of the Department of Mechanical Engineering at the University of Michigan, states in his book entitled *Thermodynamics* that "A final point should be made regarding the work done by an open system: Matter crosses the boundary of the system, and in so doing, a certain amount of energy crosses the boundary of the system. Our definition of work does not include this energy.!f

The question of the definition of work in the case of an open system has been discussed by the present author v/ith Professor R.L. Wild of the Physics Department at the University of California at Riverside. In this discussion we supposed that in a thermostat filled with water there was a cylinder closed at both ends by pistons and containing a fluid of constant composition (Figure II-A-2). In Figure II-A-2

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[12] Morey, G.V., op. **cit.,** p. 434.

[13] Goranson, R.W., op. **cit.,** pp. 39, 44.

[14] **Moelvyn-Hushes,** E.A., op. **cit.,** p.. 287.

[15] Wheeler, L.P., op. cit., p. 76.

[16] Van 'u'ylen, G.J., *Thermodynamics,* John Wiley and Sons, Inc., !k*w York, l959, p. 49.

the two arrows indicated the position of a fixed circular line around the cylinder. The fluid between the two pistons constituted a closed system and at this stage the temperature, pressure, and volume of the total mass of fluid were kept constant. We next supposed that the two pistons were moved slowly to the left in unison from the positions indicated in Figure II-A-2 by solid lines to the positions indicated by dotted lines. The mass of fluid to the left of the arrows then had received an addition and that to the right of the arrows had undergone a diminution. The mass of fluid to the left of the arrows constituted an open system which we designated as system I. Likewise, the mass of fluid to the right of the arrows constituted a second open system which we designated as system II. Systems I and II together made up a closed system, the energy of which remained constant. The energy of system I, U^I, had increased by an amount equal to the specific energy of the fluid times the mass of the fluid that had been moved past the arrows from right to left, and the energy of system II, U^{II}, had decreased by the same amount. Thus we had

$$dU^I = \breve{U}dM^I, \qquad \text{(II-A-10)}$$

$$dU^{II} = \breve{U}dM^{II} = -\breve{U}dM^I, \qquad \text{(II-A-11)(II-A-12)}$$

and

$$dU^I + dU^{II} = 0, \qquad \text{(II-A-13)}$$

where $\breve{U}$ denotes the specific energy of the fluid, and M^I and M^{II} denote the masses of open systems I and II. In the case of the open one-component system, system I, work was certainly done by the fluid on the piston at the left hand end equal to the pressure times the increase in volume

$$dW^1 = p\breve{V}dM^1, \qquad \text{(II-A-14)}$$

where p denotes the pressure of the fluid, and V denotes the specific volume of the fluid. Since the change in energy of system I was $\breve{U}dM^1$ and work was done by system I equal to $p\breve{V}dM^1$, the amount of energy that came across the fixed boundary with the incoming mass was $\breve{U}dM^1 + p\breve{V}dM^1$ which was equal to $\breve{H}dM^1$. According to Van Wylen[17] none of the energy represented by the term $\breve{H}dM^1$ is to be considered as work and this was confirmed by Professor Wild. Thus we had

$$dU^1 = \breve{H}dM^1 - dF^1, \qquad \text{(II-A-15)}$$ [18]

The major new physical decision that has to be made if the definition of work is to be extended from the case of a closed system to the case of an open system is whether or not it can be said that work is done at a fixed boundary surface across which mass is transported. Van Wylen and Professor Wild have concluded that it cannot be said that work is done at a fixed boundary surface across which mass is transported.

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[17] fan Wylen, op. cit., pp. 49, 75-77, 80.

[18] Hall and Ibele in their treatise entitled *Engineering Thermodynamics* (Prentice-Kail, Inc., Englewood Cliffs, N,J., 1960) stated on page 108 that "A general equation for energy change in an open system can be written

$$dE = dQ - dW + \sum_i (e + pv)_i dm_i. \qquad \text{(7.25)"}$$

This equation reduces to equation (II-A-15) in the case of a transfer of mass of constant composition at constant temperature and constant pressure, in which case $dQ = 0$.

Sage,[19] on the other hand, stated that in the case of an system of constant composition if the material added to ;ystem is at the same pressure as that of the system the litesimal amount of work w is given by the equation

$$w + j = pdV - p\breve{V}dm. \tag{3.18}$$

lis equation j represents frictional work (which would :e to zero in a reversible change). Sage[20] stated further- an open system is one for which material is transported JS the boundaries. Sage's equation (3.18) is thus ided to be applicable to open system I of Figure II-A-2, lis case V is a function of T, p, and m and

$$dV = \frac{\partial V}{\partial T}dT + \frac{\partial V}{\partial p}dp + \frac{\partial V}{\partial m}dm \tag{II-A-16}$$

furthermore

$$\frac{V}{m} = \breve{V} . \tag{II-A-17}$$

according to Sage

$$w + j = p\frac{\partial V}{\partial T}dT + p\frac{\partial V}{\partial p}dp + p\breve{V}dm - p\hat{V}dm$$

$$= p\frac{\partial V}{\partial T}dT + p\frac{\partial V}{\partial p}dp . \tag{XI-A-18}$$

:he transfer of material of constant composition is at

Sage, B.H., *Thermodynamics of Multicomponent Systems,* ihold Publishing Corp., New York, 1965, p. 47.

Sage, B.H., op. cit., p. 46.

constant temperature and constant pressure according to Sage $w + j = 0$. Thus in the case of open system I discussed on page 82 according to Sage $w + j = 0$, Since open system I for certain performed work $p\breve{V}dM^{\wedge}$ against the enclosing piston Sage's conclusion requires that the $p\breve{V}dM^{\wedge}$ part of the $\breve{H}dM^{\wedge}$ term be considered as work offsetting the work done by open system I against the enclosing piston. In other words, Sage[21] considers part of the energy associated with the mass transferred across the fixed boundary to be work, contrary to the conclusion of Van Wylen, Goranson, and Professor Wild. The decision between these conflicting views is one to be made by physicists and engineers and is, I believe, of some interest, but so far as I am aware, all of the thermodynamic relations and measurements needed in physical chemistry can be obtained without involving any such decision or any definition of work in the case of an open system.[22]

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[21] Sage (op. cit., p. 47) stated that "This definition of work for a constant-composition system of variable weight differs markedly from that used by Gibbs and Goranson." According to Sage, work is defined by these authors for cases in which j is zero as follows:

$$w = pdV = mp\left[\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,m} dT + \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,m} dp\right] + p\breve{V}dm \ .$$

This statement is correct as far as Goranson is concerned, but in regard to Gibbs it is not correct, since Gibbs nowhere mentioned work or heat in connection with an open system in his memoir entitled "On the Equilibrium of Heterogeneous Substances."

[22] The definition of work in the case of open systems has been of interest chiefly to engineers concerned with flow processes (see, for example, J. H. Keenan, *Thermodynamics,* John Wiley and Sons, Inc., New York, 1948, p. 35).

In accordance with the conclusion of Van Wylen, Goranson, and Professor Wild, the work W done by a one-component system of one phase and of variable mass can thus be represented by the line integral

$$W = \int_{T_0, p_0, M_0}^{T, p, M} \left\{ p \left(\frac{\partial V}{\partial T}\right)_p dT + p \left(\frac{\partial V}{\partial p}\right)_T dp + p\check{V} dM \right\}. \qquad \text{(II-A-19)}$$

This equation for work in the case of an open one-component system of one phase or the corresponding differential form

$$dW = p \left(\frac{\partial V}{\partial T}\right)_p dT + p \left(\frac{\partial V}{\partial p}\right)_T dp + p\check{V} dM , \qquad \text{(II-A-20)}$$

has been found to be of use in some engineering problems.

Appendix B to Part II

Transformation of the work and heat line integrals from one coordinate space to other coordinate spaces in the case of a one-component system of one phase and of variable mass

In Part II it was shown that it is not necessary to define either work or heat in the case of an open system of one component and of one phase when mass is being transferred to or from the system in order to obtain the energy and the entropy as functions of the absolute thermodynamic temperature, the pressure, and the total mass from experimental measurements. Thus the derivation of the Jacobians listed in Tables II-l to 11-15 did not depend upon definitions of work or heat in the case of an open system of one component and of one phase when mass is being transferred to or from the system.

For some purposes, however, it is useful to have definitions of work and heat in the case of an open system of one component and of one phase when mass is being transferred to or from the system as was shown in Appendix A to Part II. The derivatives of the work done by a system of one component and one phase and of variable mass are total derivatives with respect to the variables chosen as the parameters defining the paths of the integral. In order to obtain the total derivative of the work done along a straight line parallel to one of the coordinate axes in any coordinate space one obtains from Tables II-l to 11-15 the partial derivative of the volume with respect to the quantity plotted along that axis when the quantitites plotted along the other axes are held .constant and one multiplies this partial derivative by the pressure.

The derivatives of the heat received by a system of one component and one phase and of variable mass are also total derivatives with respect to the variables chosen as the parameters defining the paths of the integral. However, the derivatives of the heat received by a one-component system of one phase and of variable mass along straight lines parallel to the coordinate axes in various coordinate spaces cannot be obtained by multiplication of the' partial derivatives of the entropy by the absolute thermodynamic temperature when transfer of masses to or from the system are involved. In such cases the total derivatives of the heat received along lines parallel to the coordinate axes in any desired coordinate space can be derived in terns of the total derivatives of the heat received along lines parallel to the coordinate axes in (7\ p, A/)-space by transformation of the heat line integrals as explained in the second half of Appendix C to Part II. Following is an example of such a transformation. In the case of a one-component system of one phase and of variable mass the heat line integral extended along a path in (7\ *M** F)-space is

$$Q = \int_{T_0, M_0, V_0}^{T, M_9 V} \left\{ \frac{dQ}{dT} dT + \frac{dQ}{dM} dM + \frac{dQ}{dV} dV \right\}$$

$$= \int^{r, M, V} \left\{ M\breve{c}_V dT + \frac{dQ}{dN} dM + l_V dV \right\} . \qquad \text{(II-B-1)}$$

In order to transform this integral to (T, p, M)-space we make use of equations (II-C-63), (II-C-64), and (II-C-65) in Appendix C to Part II. For the purpose of substitution of values in equations (II-C-63), (II-C-64) and (II-C-65) the equivalence of symbols is given in the following Table.

Table II-B-1

Equivalence of symbols

Γ	Q
x	T
y	M
z	V
$\left(\frac{d\Gamma}{dx}\right)_{y,z}$	$\left(\frac{dQ}{dT}\right)_{M,V}$
$\left(\frac{d\Gamma}{dy}\right)_{x,z}$	$\left(\frac{dQ}{dM}\right)_{T,V}$
$\left(\frac{d\Gamma}{dz}\right)_{x,y}$	$\left(\frac{dQ}{dV}\right)_{T,M}$
u	T
v	p
w	M
$\left(\frac{d\Gamma}{du}\right)_{v,w}$	MC_p
$\left(\frac{d\Gamma}{dv}\right)_{u,w}$	Ml_p
$\left(\frac{d\Gamma}{dw}\right)_{u,v}$	0

Substituting the values from Table II-B-1 in equation (II-C-63) we have

$$\left(\frac{\partial Q}{\partial T}\right)_{M,V} = M\breve{c}_V = \frac{\begin{vmatrix} M\breve{c}_p & M\breve{l}_p & 0 \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \end{vmatrix}}{\begin{vmatrix} \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \end{vmatrix}}, \qquad \text{(II-B-2)}$$

and multiplying out the quantities in the determinants we obtain

$$\left(\frac{\partial Q}{\partial T}\right)_{M,V} = M\breve{c}_V = \left[M \breve{c}_p \ldots \left(\frac{\partial \breve{v}}{\partial p}\right)_T \ldots \left(\frac{\partial \breve{v}}{\partial T}\right)_p \ldots \left(\frac{\partial \breve{v}}{\partial p}\right)_T \right] \qquad \text{(II-3-3)}$$

Similarly, substituting the values from Table II-3-1 in equation (II-C-64) we have

$$\left(\frac{dQ}{dM}\right)_{T,V} = \frac{\begin{vmatrix} M\breve{c}_p & N\breve{i}p & 0 \\ \frac{dT}{dT} & \frac{dT}{dp} & \frac{dT}{dM} \\ \frac{dV}{dT} & \frac{dv}{dp} & \frac{dV}{dM} \end{vmatrix}}{\begin{vmatrix} \frac{dM}{dT} & \frac{dM}{dp} & \frac{dM}{dM} \\ \frac{dT}{dT} & \frac{dT}{dp} & \frac{dT}{dM} \\ \frac{dV}{dT} & \frac{dV}{dp} & \frac{dV}{dM} \end{vmatrix}} , \qquad \text{(II-B-4)}$$

and multiplying out the quantities in the determinants we obtain

$$\left(\frac{dQ}{dM}\right)_{4.P-} = \left[-\dot{h}\, r_p 11 \,\partial M\right] \div \left[\frac{\partial V}{\partial p}\right]$$

$$= \left[T\breve{V}\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right] \div \left(\frac{\partial \breve{V}}{\partial p}\right)_T . \qquad \text{(II-B-5)}$$

Finally, substituting the values from Table II-B-1 in equation (II-C-65) we have

$$\left(\frac{\partial Q}{\partial V}\right)_{T,M} = l_v = \frac{\begin{vmatrix} M\breve{c}_p & M\breve{l}_p & 0 \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \end{vmatrix}}{\begin{vmatrix} \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial M} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial M} \\ \frac{\partial M}{\partial T} & \frac{\partial M}{\partial p} & \frac{\partial M}{\partial M} \end{vmatrix}}, \qquad \text{(II-B-6)}$$

and multiplying out the quantities in the determinants we obtain

$$\left(\frac{\partial Q}{\partial V}\right)_{T,M} = l_v = \left[-M\breve{l}_p\right] \div \left[-\frac{\partial V}{\partial p}\right]$$

$$= \left[-T\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right] \div \left(\frac{\partial \breve{V}}{\partial p}\right)_T , \qquad \text{(II-B-7)}$$

The corresponding values of the partial derivatives of the entropy obtained from Tables 11-10, II-3, and II-2 are

$$\left(\frac{\partial S}{\partial T}\right)_{[illegible]} = \left[\breve{C}_p \left(\frac{\partial \breve{V}}{[illegible]}\right) [illegible] \left(\frac{\partial \breve{V}}{[illegible]}\right)^2\right] [illegible] \left(\frac{\partial \breve{V}}{[illegible]}\right)_T \qquad \text{[illegible]}$$

$$\left(\frac{\partial S}{\partial M}\right)_{[illegible]} = \left[\breve{V}\left(\frac{\partial \breve{V}}{\partial T}\right)_p + \breve{S}\left(\frac{\partial \breve{V}}{\partial p}\right)_T\right] \div \left(\frac{\partial \breve{V}}{\partial p}\right)_T , \qquad \text{(II-B-9)}$$

and

$$\left(\frac{\partial S}{[illegible]}\right)_{[illegible]} = \left[-\left(\frac{\partial \breve{V}}{\partial T}\right)_p\right] \div \left(\frac{\partial \breve{V}}{\partial p}\right)_T . \qquad \text{(II-B-10)}$$

Thus it follows from (XI-B-3), (II-B-7), (II-B-8), and (II-B-10) that

$$\left(\frac{dQ}{dT}\right)_{M,\,V} = T\left(\frac{\partial S}{\partial T}\right)_{M,\,V} \qquad \text{(II-B-11)}$$

and

$$\left(\frac{dQ}{dV}\right)_{[illegible]} = T\left(\frac{\partial S}{\partial V}\right)_{T,\,M} , \qquad \text{(II-B-12)}$$

but, finally, it also follows from (II-B-5) and (II-B-9) that

$$\left([illegible]\right)_{[illegible],\,V} = T\left(\frac{\partial S}{[illegible]}\right)_{T,\,V} \qquad \text{[illegible]}$$

Appendix C to Part II

Proofs of the relations:

$$\left(\frac{\partial x'}{\partial x}\right)_{y,\,z} = \frac{\dfrac{\partial(x',\,y,\,z)}{\partial(u,\,v,\,w)}}{\dfrac{\partial(x,\,y,\,z)}{\partial(u,\,v,\,w)}}$$

and

$$\left(\frac{\partial x'}{\partial x}\right)_{y,\,z} = \frac{\begin{vmatrix} \dfrac{\partial x'}{\partial u} & \dfrac{\partial x'}{\partial v} & \dfrac{\partial x'}{\partial w} \\ \dfrac{\partial y}{\partial u} & \dfrac{\partial y}{\partial v} & \dfrac{\partial y}{\partial w} \\ \dfrac{\partial z}{\partial u} & \dfrac{\partial z}{\partial v} & \dfrac{\partial z}{\partial w} \end{vmatrix}}{\begin{vmatrix} \dfrac{\partial x}{\partial u} & \dfrac{\partial x}{\partial v} & \dfrac{\partial x}{\partial w} \\ \dfrac{\partial y}{\partial u} & \dfrac{\partial y}{\partial v} & \dfrac{\partial y}{\partial w} \\ \dfrac{\partial z}{\partial u} & \dfrac{\partial z}{\partial v} & \dfrac{\partial z}{\partial w} \end{vmatrix}}$$

It is assumed that x' is a function of x, y, and z

$$x' = \psi(x, y, z), \qquad \text{(II-C-1)}$$

and that x, y, and z are functions of u, v, and w

$$x = f(u, v, w), \qquad \text{(II-C-2)}$$
$$y = \phi(u, v, w), \qquad \text{(II-C-3)}$$
$$z = \chi(u, v, w). \qquad \text{(II-C-4)}$$

It is assumed further that these functions are continuous together with their first partial derivatives. By application of the theorem for change of variables in partial differentiation one then obtains

$$\frac{\partial x'}{\partial u} = \frac{\partial x'}{\partial x}\frac{\partial x}{\partial u} + \frac{\partial x'}{\partial y}\frac{\partial y}{\partial u} + \frac{\partial x'}{\partial z}\frac{\partial z}{\partial u} , \qquad \text{(II-C-5)}$$

$$\frac{\partial x'}{\partial v} = \frac{\partial x'}{\partial x}\frac{\partial x}{\partial v} + \frac{\partial x'}{\partial y}\frac{\partial y}{\partial v} + \frac{\partial x'}{\partial z}\frac{\partial z}{\partial v} , \qquad \text{(II-C-6)}$$

and

$$\frac{\partial x'}{\partial w} = \frac{\partial x'}{\partial x}\frac{\partial x}{\partial w} + \frac{\partial x'}{\partial y}\frac{\partial y}{\partial w} + \frac{\partial x'}{\partial z}\frac{\partial z}{\partial w} . \qquad \text{(II-C-7)}$$

From equations (II-C-5), (II-C-6) and (II-C-7) it follows that

$$\frac{\partial x'}{\partial z}\frac{\partial z}{\partial u} = -\frac{\partial x'}{\partial x}\frac{\partial x}{\partial u} - \frac{\partial x'}{\partial y}\frac{\partial y}{\partial u} + \frac{\partial x'}{\partial u} , \qquad \text{(II-C-8)}$$

$$\frac{\partial x'}{\partial z}\frac{\partial z}{\partial v} = -\frac{\partial x'}{\partial x}\frac{\partial x}{\partial v} - \frac{\partial x'}{\partial y}\frac{\partial y}{\partial v} + \frac{\partial x'}{\partial v} , \qquad \text{(II-C-9)}$$

and

$$\frac{\partial x'}{\partial z}\frac{\partial z}{\partial w} = -\frac{\partial x'}{\partial x}\frac{\partial x}{\partial w} - \frac{\partial x'}{\partial y}\frac{\partial y}{\partial w} + \frac{\partial x'}{\partial w} , \qquad \text{(II-C-10)}$$

Dividing both sides of equation (II-C-8) by $\frac{\partial z}{\partial u}$, and both sides of equation (II-C-9) by $\frac{\partial z}{\partial v}$, likewise both sides of equation (II-C-10) by $\frac{\partial z}{\partial w}$ we have

$$\frac{\partial y}{\partial z} = \frac{\frac{\partial x'}{\partial u} - \frac{\partial y}{\partial x}\frac{\partial x}{\partial u} - \frac{\partial y}{\partial y}\frac{\partial x}{\partial u}}{\frac{\partial z}{\partial u}}, \tag{II-C-11}$$

$$\frac{\partial x'}{\partial z} = \frac{\frac{\partial y}{\partial v} - \frac{\partial y}{\partial x}\frac{\partial x}{\partial v} - \frac{\partial x'}{\partial y}\frac{\partial y}{\partial v}}{\frac{\partial z}{\partial v}}, \tag{II-C-12}$$

and

$$\frac{\partial y}{\partial z} = \frac{\frac{\partial y}{\partial w} - \frac{\partial y}{\partial x}\frac{\partial x}{\partial w} - \frac{\partial y}{\partial y}\frac{\partial x}{\partial w}}{\frac{\partial z}{\partial w}}. \tag{II-C-13}$$

It follows that the right side of equation (II-C-11) is equal to the right side of equation (II-C-12)

$$\frac{\frac{\partial x'}{\partial u} - \frac{\partial y}{\partial x}\frac{\partial x}{\partial u} - \frac{\partial x'}{\partial y}\frac{\partial y}{\partial u}}{\frac{\partial z}{\partial u}} = \frac{\frac{\partial y}{\partial v} - \frac{\partial y}{\partial x}\frac{\partial x}{\partial v} - \frac{\partial y}{\partial y}\frac{\partial y}{\partial v}}{\frac{\partial z}{\partial v}}. \tag{II-C-14}$$

Multiplying both sides of equation (II-C-14) by $\left(\frac{\partial z}{\partial v}\frac{\partial z}{\partial u}\right)$ we have

$\frac{\partial z}{\partial v}\Big(\frac{\partial x'}{\partial u} - \frac{\partial x'}{\partial x}$ 3u " 3y 3u/ " *du\dv " dx dv* $\frac{\partial x'}{\partial x}\frac{\partial x}{\partial v}$ $\frac{\partial x'}{dy}\frac{\partial y}{dv}\Big)$.(II-C-15)

Likewise it follows that the right side of equation (II-C-12) is equal to the right side of equation (II-C-13)

$\frac{\partial x'}{dv}$ — ∂ ^1x/3x dv — ∂^ lz/dy 3v, over $\frac{\partial z}{dv}$

(II-C-16)

= 3x[/dw — 3//dx 3x/dw ^ 3^/dy 3^/dw, over dz/dv/ .

Multiplying both sides of equation (II-C-16) by (f-^-^-j) we have

$\frac{\partial z}{\partial w}\Big(\frac{\partial x'}{\partial v} - \frac{\partial x'}{\partial x}\frac{\partial x}{\partial v}$ - d^d^\ dy dv) = 3z/3^ dv\dw ~ 3xJ/dx 3x/dw ~ j ^/dy $\frac{\partial y}{\partial w}\Big)$.(II-C-17)

Consequently ve have from equations (II-C-15) and (II-C-17)

3v 3u " *dv dx du ' dv dy du " du dv "* 3u *dx dv* 3u *dy dv '*
(II-C-18)

and

$\frac{\partial z}{\partial w}\frac{\partial x'}{\partial v} - \frac{\partial z}{\partial w}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial v} - \frac{\partial z}{\partial w}\frac{\partial x'}{\partial y}\frac{\partial y}{\partial v} = \frac{\partial z}{\partial v}\frac{\partial x'}{\partial w} - \frac{\partial z}{\partial v}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial w}$ - ∂ ∂v 3y 3v *
(II-C-19)

From equation (II-C-18) it follows that

$$\frac{\partial x'}{\partial y}\frac{\partial z}{\partial u}\frac{\partial y}{\partial v} - \frac{\partial x'}{\partial y}\frac{\partial z}{\partial v}\frac{\partial y}{\partial u} = \frac{\partial z}{\partial u}\frac{\partial x'}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial x'}{\partial u} + \frac{\partial z}{\partial v}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial u} - \frac{\partial z}{\partial u}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial v} \qquad \text{(II-C-20)}$$

and from equation (II-C-19) it follows that

$$\frac{\partial x'}{\partial y}\frac{\partial z}{\partial v}\frac{\partial y}{\partial w} - \frac{\partial x'}{\partial y}\frac{\partial z}{\partial w}\frac{\partial y}{\partial v} = \frac{\partial z}{\partial v}\frac{\partial x'}{\partial w} - \frac{\partial z}{\partial w}\frac{\partial x'}{\partial v} + \frac{\partial z}{\partial w}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial w} \qquad \text{(II-C-21)}$$

Dividing both sides of equation (II-C-20) by $\left(\frac{\partial z}{\partial u}\frac{\partial y}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial y}{\partial u}\right)$ we have

$$\frac{\partial x'}{\partial y} = \frac{\frac{\partial z}{\partial u}\frac{\partial x'}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial x'}{\partial u} + \frac{\partial z}{\partial v}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial u} - \frac{\partial z}{\partial u}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial v}}{\frac{\partial z}{\partial u}\frac{\partial y}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial y}{\partial u}} \qquad \text{(II-C-22)}$$

and dividing both sides of equation (II-C-21) by $\left(\frac{\partial z}{\partial v}\frac{\partial y}{\partial w} - \frac{\partial z}{\partial w}\frac{\partial y}{\partial v}\right)$ we have

$$\frac{\partial x'}{\partial y} = \frac{\frac{\partial z}{\partial v}\frac{\partial x'}{\partial w} - \frac{\partial z}{\partial w}\frac{\partial x'}{\partial v} + \frac{\partial z}{\partial w}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial x'}{\partial x}\frac{\partial x}{\partial w}}{\frac{\partial z}{\partial v}\frac{\partial y}{\partial w} - \frac{\partial z}{\partial w}\frac{\partial y}{\partial v}} \qquad \text{(II-C-23)}$$

Consequently the right side of equation (II-C-22) is equal to the right side of equation (II-C-23)

$$\frac{\dfrac{\partial z}{\partial u}\dfrac{\partial x'}{\partial v} - \dfrac{\partial z}{\partial v}\dfrac{\partial x'}{\partial u} + \dfrac{\partial z}{\partial v}\dfrac{\partial x'}{\partial x}\dfrac{\partial x}{\partial u} - \dfrac{\partial z}{\partial u}\dfrac{\partial x'}{\partial x}\dfrac{\partial x}{\partial v}}{\dfrac{\partial z}{\partial u}\dfrac{\partial y}{\partial v} - \dfrac{\partial z}{\partial v}\dfrac{\partial y}{\partial u}}$$

$$= \frac{\dfrac{\partial z}{\partial v}\dfrac{\partial x'}{\partial w} - \dfrac{\partial z}{\partial w}\dfrac{\partial x'}{\partial v} + \dfrac{\partial z}{\partial w}\dfrac{\partial x'}{\partial x}\dfrac{\partial x}{\partial v} - \dfrac{\partial z}{\partial v}\dfrac{\partial x'}{\partial x}\dfrac{\partial x}{\partial w}}{\dfrac{\partial z}{\partial v}\dfrac{\partial y}{\partial w} - \dfrac{\partial z}{\partial w}\dfrac{\partial y}{\partial v}} \,. \qquad \text{(II-C-24)}$$

Multiplying both sides of equation (II-C-24) by $\left(\frac{\partial z}{\partial v}\frac{\partial y}{\partial w} - \frac{\partial z}{\partial w}\frac{\partial y}{\partial v}\right)\left(\frac{\partial z}{\partial u}\frac{\partial y}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial y}{\partial u}\right)$, we have

$$\left(\frac{\partial z}{\partial v}\frac{\partial y}{\partial w} - \frac{\partial z}{\partial w}\frac{\partial y}{\partial v}\right)\left(\frac{\partial z}{\partial u}\frac{\partial x'}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial x'}{\partial u} + \frac{\partial x'}{\partial x}\frac{\partial z}{\partial v}\frac{\partial x}{\partial u} - \frac{\partial x'}{\partial x}\frac{\partial z}{\partial u}\frac{\partial x}{\partial v}\right)$$

$$= \left(\frac{\partial z}{\partial u}\frac{\partial y}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial y}{\partial u}\right)\left(\frac{\partial z}{\partial v}\frac{\partial x'}{\partial w} - \frac{\partial z}{\partial w}\frac{\partial x'}{\partial v} + \frac{\partial x'}{\partial x}\frac{\partial z}{\partial w}\frac{\partial x}{\partial v} - \frac{\partial x'}{\partial x}\frac{\partial z}{\partial v}\frac{\partial x}{\partial w}\right). \qquad \text{(II-C-25)}$$

Consequently it follows that

$$\frac{\partial x'}{\partial x}\left(\frac{\partial z}{\partial v}\frac{\partial x}{\partial u} - \frac{\partial z}{\partial u}\frac{\partial x}{\partial v}\right)\left(\frac{\partial z}{\partial v}\frac{\partial y}{\partial w} - \frac{\partial z}{\partial w}\frac{\partial y}{\partial v}\right)$$

$$+\left(\frac{\partial z}{\partial u}\frac{\partial x'}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial x'}{\partial u}\right)\left(\frac{\partial z}{\partial v}\frac{\partial y}{\partial w} - \frac{\partial z}{\partial w}\frac{\partial y}{\partial v}\right) \qquad \text{(II-C-26)}$$

$$-\frac{\partial x'}{\partial x}\left(\frac{\partial z}{\partial w}\frac{\partial x}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial x}{\partial w}\right)\left(\frac{\partial z}{\partial u}\frac{\partial y}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial y}{\partial u}\right)$$

$$-\left(\frac{\partial z}{\partial v}\frac{\partial x'}{\partial w} - \frac{\partial z}{\partial w}\frac{\partial x'}{\partial v}\right)\left(\frac{\partial z}{\partial u}\frac{\partial y}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial y}{\partial u}\right)$$

$$= 0 \,.$$

Equation (II-C-26) is then solved for $\frac{\partial x'}{\partial x}$ and we thus obtain

$$\frac{\partial x'}{\partial x} = \frac{\left[\left(\frac{\partial z}{\partial v}\frac{\partial x'}{\partial w} - \frac{\partial z}{\partial w}\frac{\partial x'}{\partial v}\right)\left(\frac{\partial z}{\partial u}\frac{\partial y}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial y}{\partial u}\right) - \left(\frac{\partial z}{\partial u}\frac{\partial x'}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial x'}{\partial u}\right)\left(\frac{\partial z}{\partial v}\frac{\partial y}{\partial w} - \frac{\partial z}{\partial w}\frac{\partial y}{\partial v}\right)\right]}{\left[\left(\frac{\partial z}{\partial v}\frac{\partial x}{\partial u} - \frac{\partial z}{\partial u}\frac{\partial x}{\partial v}\right)\left(\frac{\partial z}{\partial v}\frac{\partial y}{\partial w} - \frac{\partial z}{\partial w}\frac{\partial y}{\partial v}\right) - \left(\frac{\partial z}{\partial w}\frac{\partial x}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial x}{\partial w}\right)\left(\frac{\partial z}{\partial u}\frac{\partial y}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial y}{\partial u}\right)\right]} \quad \text{(II-C-27)}$$

Multiplying out the expressions in parentheses in equation (II-C-27) we have

$$\frac{\partial x'}{\partial x} = \frac{\left[\frac{\partial z}{\partial v}\frac{\partial x'}{\partial w}\frac{\partial z}{\partial u}\frac{\partial y}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial x'}{\partial w}\frac{\partial z}{\partial v}\frac{\partial y}{\partial u} - \frac{\partial z}{\partial w}\frac{\partial x'}{\partial v}\frac{\partial z}{\partial u}\frac{\partial y}{\partial v} + \frac{\partial z}{\partial w}\frac{\partial x'}{\partial v}\frac{\partial z}{\partial v}\frac{\partial y}{\partial u} - \frac{\partial z}{\partial u}\frac{\partial x'}{\partial v}\frac{\partial z}{\partial v}\frac{\partial y}{\partial w} + \frac{\partial z}{\partial u}\frac{\partial x'}{\partial v}\frac{\partial z}{\partial w}\frac{\partial y}{\partial v} + \frac{\partial z}{\partial v}\frac{\partial x'}{\partial u}\frac{\partial z}{\partial v}\frac{\partial y}{\partial w} - \frac{\partial z}{\partial v}\frac{\partial x'}{\partial u}\frac{\partial z}{\partial w}\frac{\partial y}{\partial v}\right]}{\left[\frac{\partial z}{\partial v}\frac{\partial x}{\partial u}\frac{\partial z}{\partial v}\frac{\partial y}{\partial w} - \frac{\partial z}{\partial v}\frac{\partial x}{\partial u}\frac{\partial z}{\partial w}\frac{\partial y}{\partial v} - \frac{\partial z}{\partial u}\frac{\partial x}{\partial v}\frac{\partial z}{\partial v}\frac{\partial y}{\partial w} + \frac{\partial z}{\partial u}\frac{\partial x}{\partial v}\frac{\partial z}{\partial w}\frac{\partial y}{\partial v} - \frac{\partial z}{\partial w}\frac{\partial x}{\partial v}\frac{\partial z}{\partial u}\frac{\partial y}{\partial v} + \frac{\partial z}{\partial w}\frac{\partial x}{\partial v}\frac{\partial z}{\partial v}\frac{\partial y}{\partial u} + \frac{\partial z}{\partial v}\frac{\partial x}{\partial w}\frac{\partial z}{\partial u}\frac{\partial y}{\partial v} - \frac{\partial z}{\partial v}\frac{\partial x}{\partial w}\frac{\partial z}{\partial v}\frac{\partial y}{\partial u}\right]}, \quad \text{(II-C-28)}$$

Now the third term in the bracket constituting the numerator of the right side of equation (II-C-28) cancels the sixth term in this bracket. Likewise the fourth term in the bracket constituting the denominator of the right side of equation (II-C-28) cancels the fifth term in this bracket. The remaining terms in the numerator and denominator of the right side of equation (II-C-28) have a common factor $\frac{\partial z}{\partial w}$ which we next divide out. The terms that are then left are equivalent to the quotient of two Jacobian determinants. We thus have

$$\left(\frac{\partial x'}{\partial x}\right)_{y,\,z} = \frac{\begin{vmatrix} \frac{\partial x'}{\partial u} & \frac{\partial x'}{\partial v} & \frac{\partial x'}{\partial w} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \\ \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \end{vmatrix}}{\begin{vmatrix} \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} & \frac{\partial x}{\partial w} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \\ \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \end{vmatrix}} , \qquad \text{(II-C-29)}$$

provided the Jacobian determinant in the denominator is not equal to zero. Thus we obtain the result

$$\left(\frac{\partial x'}{\partial x}\right)_{y,\,z} = \frac{\frac{\partial(x',\, y,\, z)}{\partial(u,\, v,\, w)}}{\frac{\partial(x,\, y,\, z)}{\partial(u,\, v,\, w)}} . \qquad \text{(II-C-30)}$$

Similarly we have

$$\left(\frac{\partial x'}{\partial y}\right)_{x,\,z} = \frac{\frac{\partial(x',\, x,\, z)}{\partial(u,\, v,\, w)}}{\frac{\partial(y,\, x,\, z)}{\partial(u,\, v,\, w)}} . \qquad \text{(II-C-31)}$$

and

$$\left(\frac{\partial x'}{\partial z}\right)_{x,y} = \frac{\dfrac{\partial(x', x, y)}{\partial(u, v, w)}}{\dfrac{\partial(z, x, y)}{\partial(u, v, w)}} \; . \qquad \text{(II-C-32)}$$

Equations (II-C-30), (II-C-31), and (II-C-32) are not applicable, however, in the case of a one-component system of one phase and of variable mass when it is desired to transform the heat line integral from one coordinate space, such as the temperature-volume-mass coordinate space, to another coordinate space, such as the temperature-pressure-mass coordinate space, because the heat line integral depends upon the path and is not a function of the coordinates. In this case, to which the second equation of the heading of this Appendix applies, the transformation can be accomplished in the following way. Let us suppose that a line integral T

$$T = \int_{x_0, y_0, z_0}^{x, y, z} [P(x, y, z)dx + Q(x, y, z)dy + R(x, y, z)dz] \qquad \textbf{(II-C-33)}$$

depends upon the path, in which case, $\frac{\partial P}{\partial y} \neq \frac{\partial Q}{\partial x}$, $\frac{\partial P}{\partial z} \neq \frac{\partial R}{\partial x}$, and $\frac{\partial Q}{\partial z} \neq \frac{\partial R}{\partial y}$. This integral has no meaning unless further relations are given defining a particular path in (x, y, z)-space. For example, the curve can be represented in parametric form by the equations, $x = f(\sigma)$, $y = \phi(\sigma)$, and z = 5(o). We are next given that x» *y,* and *z* are functions of ii, *v₉* and *w₉*

x = <£(u, v, *w)f* *y* = x(ut v, *w),* *z* = ^(u, v, *w).* (II-C-34) (II-C-35) (II-C-36)

It is then desired to transform the integral *T* from (x, y* z)-space to (uf K, uO-space. In this case if equations (II-C-34), (II-C-35), and (II-C-36) can be solved so that we have

a = *(x, *y, z),* *v* = X(x, y, z), u^ = *(x, y, z), (II-C-37) (II-C-38) (II-C-39)

then the curve in (x, y, z)-space can be transformed into the curve in (u, v, *w)-space* defined by the equations *u = F(s),* *v* = A(5), and v = 5(s). We next replace *dx* in the integral *T*

by ^ *du* +^ *dv* + ^ *dw* , also dy by |* du + |^ *dv* + |^ dv
ou dv dv/ f ^ J du du 8^

and *dz by* $\frac{\partial z}{\partial u}$ du + $\frac{\partial z}{\partial v}$ *dv* + $\frac{\partial z}{\partial w}$ d^« We then have

$$\Gamma = \int^{u,v,w} \left\{ P\left[\frac{\partial x}{\partial u}du + \frac{\partial x}{\partial v}dv + \frac{\partial x}{\partial w}dw\right] + Q\left[\frac{\partial y}{\partial u}du + \frac{\partial y}{\partial v}dv + \frac{\partial y}{\partial w}dw\right] + R\left[\frac{\partial z}{\partial u}du + \frac{\partial z}{\partial v}dv + \frac{\partial z}{\partial w}dw\right]\right\}, \qquad \text{(II-C-40)}$$

the curve in **(uf v, v)-space** mow **being determined** by the equations $u = F(s)$, $v = G(s)$, $w = H(s)$. Consequently we thus obtain

$$T = \int_{u_0,\, v_0,\, w_0}^{u,\, v,\, w} \left\{ P(\phi(u, v, w), \chi(u, v, w), \psi(u, v, w)) \left[\frac{\partial x}{\partial u} du + \frac{\partial x}{\partial v} dv + \frac{\partial x}{\partial w} dw \right] \right.$$

$$+ Q(\phi(u, v, w), \chi(u, v, w), \psi(u, v, w)) \left[\frac{\partial y}{\partial u} du + \frac{\partial y}{\partial v} dv + \frac{\partial y}{\partial w} dw \right]$$

$$\left. + R(\phi(u, v, w), \chi(u, v, w), \psi(u, v, w)) \left[\frac{\partial z}{\partial u} du + \frac{\partial z}{\partial v} dv + \frac{\partial z}{\partial w} dw \right] \right\}$$

$$= \int_{u_0,\, v_0,\, w_0}^{u,\, v,\, w} \left\{ \Phi(u, v, w) du + \Pi(u, v, w) dv + \Theta(u, v, w) dw \right\}, \qquad \text{(II-C-41)}$$

where Φ is set equal to

$$P(\phi(u, v, w), \chi(u, v, w), \psi(u, v, w)) \frac{\partial x}{\partial u}$$

$$+ Q(\phi(u, v, w), \chi(u, v, w), \psi(u, v, w)) \frac{\partial y}{\partial u}$$

$$+ R(\phi(u, v, w), \chi(u, v, w), \psi(u, v, w)) \frac{\partial z}{\partial u},$$

Π is set equal to

$$P(\phi(u, v, w), \chi(u, v, w), \psi(u, v, w)) \frac{\partial x}{\partial v}$$

$$+ Q(\phi(u, v, w), \chi(u, v, w), \psi(u, v, w)) \frac{\partial y}{\partial v}$$

$$\partial v ,$$

and Q is set equal to

$$P(\phi(u, v, w), \chi(u, v, w), \psi(u, v, w))\frac{\partial x}{\partial w}$$

$$+ Q(\phi(\qquad\qquad\qquad))\frac{\partial y}{\partial w}$$

$$+ R(\phi(u, v, w), \chi(u, v, w), \psi(u, v, w))\frac{\partial z}{\partial w}.$$

In order to evaluate P, Q, and R as functions of u, v, and w we next solve the equations

$$\Theta = P\frac{\partial x}{\partial u} + Q\frac{\partial y}{\partial u} + R\frac{\partial z}{\partial u}, \qquad \text{(II-C-42)}$$

$$\Pi = P\frac{\partial x}{\partial v} + Q\frac{\partial y}{\partial v} + R\frac{\partial z}{\partial v}, \qquad \text{(II-C-43)}$$

and

$$\Omega = P\frac{\partial x}{\partial w} + Q\frac{\partial y}{\partial w} + R\frac{\partial z}{\partial w}, \qquad \text{(II-C-44)}$$

for P, Q, and R. Thus we have

$$R\frac{\partial z}{\partial u} = \Theta - P\frac{\partial x}{\partial u} - Q\frac{\partial y}{\partial u}, \qquad \text{(II-C-45)}$$

$$R\frac{\partial z}{\partial v} = \Pi - P\frac{\partial x}{\partial v} - Q\frac{\partial y}{\partial v}, \qquad \text{(II-C-46)}$$

and

Dividing both sides of equation (II-C-45) by $\frac{\partial z}{\partial u}$, both sides of equation (II-C-46) by $\frac{\partial z}{\partial v}$, and both sides of equation (II-C-47) by $\frac{\partial z}{\partial w}$, we obtain

$$R = \Theta\Big/\frac{\partial z}{\partial u} - P\frac{\partial x}{\partial u}\Big/\frac{\partial z}{\partial u} - Q\frac{\partial y}{\partial u}\Big/\frac{\partial z}{\partial u} , \qquad \text{(II-C-48)}$$

$$R = \Pi\Big/\frac{\partial z}{\partial v} - P\frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v} - Q\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} , \qquad \text{(II-C-49)}$$

and

$$R = \Omega\Big/\frac{\partial z}{\partial w} - P\frac{\partial x}{\partial w}\Big/\frac{\partial z}{\partial w} - Q\frac{\partial y}{\partial w}\Big/\frac{\partial z}{\partial w} . \qquad \text{(II-C-50)}$$

Consequently we have

$$\Theta\Big/\frac{\partial z}{\partial u} - P\frac{\partial x}{\partial u}\Big/\frac{\partial z}{\partial u} - Q\frac{\partial y}{\partial u}\Big/\frac{\partial z}{\partial u} = \Pi\Big/\frac{\partial z}{\partial v} - P\frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v} - Q\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} , \qquad \text{(II-C-51)}$$

and

$$\Omega\Big/\frac{\partial z}{\partial w} - P\frac{\partial x}{\partial w}\Big/\frac{\partial z}{\partial w} - Q\frac{\partial y}{\partial w}\Big/\frac{\partial z}{\partial w} = \Pi\Big/\frac{\partial z}{\partial v} - P\frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v} - Q\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} . \qquad \text{(I-C-52)}$$

From equations (II-C-51) and (II-C-52) it follows that

$$Q\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - Q\frac{\partial y}{\partial u}\Big/\frac{\partial z}{\partial u} = \Pi\Big/\frac{\partial z}{\partial v} - \Theta\Big/\frac{\partial z}{\partial u} + P\frac{\partial x}{\partial u}\Big/\frac{\partial z}{\partial u} - P\frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v} \qquad \text{(II-C-53)}$$

and

$$Q\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - Q\frac{\partial y}{\partial w}\Big/\frac{\partial z}{\partial w} = \Pi\Big/\frac{\partial z}{\partial v} - \Omega\Big/\frac{\partial z}{\partial w} + P\frac{\partial x}{\partial w}\Big/\frac{\partial z}{\partial w} - P\frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v} . \qquad \text{(II-C-54)}$$

Dividing both sides of equation (II-C-53) by $\left(\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial u}\Big/\frac{\partial z}{\partial u}\right)$ and both sides of equation (II-C-54) by $\left(\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial w}\Big/\frac{\partial z}{\partial w}\right)$ we have

$$Q = \frac{\Pi\Big/\frac{\partial z}{\partial v} - \Theta\Big/\frac{\partial z}{\partial u} + P\left(\frac{\partial x}{\partial u}\Big/\frac{\partial z}{\partial u} - \frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v}\right)}{\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial u}\Big/\frac{\partial z}{\partial u}} \qquad \text{(II-C-55)}$$

and

$$Q = \frac{\Pi\Big/\frac{\partial z}{\partial v} - \Omega\Big/\frac{\partial z}{\partial w} + P\left(\frac{\partial x}{\partial w}\Big/\frac{\partial z}{\partial w} - \frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v}\right)}{\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial w}\Big/\frac{\partial z}{\partial w}} . \qquad \text{(II-C-56)}$$

Consequently we have

$$\frac{\Pi\Big/\frac{\partial z}{\partial v} - \Theta\Big/\frac{\partial z}{\partial u} + P\left(\frac{\partial x}{\partial u}\Big/\frac{\partial z}{\partial u} - \frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v}\right)}{\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial u}\Big/\frac{\partial z}{\partial u}}$$

$$= \frac{\Pi\Big/\frac{\partial z}{\partial v} - \Omega\Big/\frac{\partial z}{\partial w} + P\left(\frac{\partial x}{\partial w}\Big/\frac{\partial z}{\partial w} - \frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v}\right)}{\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial w}\Big/\frac{\partial z}{\partial w}} . \qquad \text{(II-C-57)}$$

Multiplying both sides of equation (II-C-57) by $\left(\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial u}\Big/\frac{\partial z}{\partial u}\right)\left(\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial w}\Big/\frac{\partial z}{\partial w}\right)$ we obtain

$$\left(\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial w}\Big/\frac{\partial z}{\partial w}\right)\left[\Pi\Big/\frac{\partial z}{\partial v} - \Theta\Big/\frac{\partial z}{\partial u} + P\left(\frac{\partial x}{\partial u}\Big/\frac{\partial z}{\partial u} - \frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v}\right)\right]$$

$$= \left(\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial u}\Big/\frac{\partial z}{\partial u}\right)\left[\Pi\Big/\frac{\partial z}{\partial v} - \Omega\Big/\frac{\partial z}{\partial w} + P\left(\frac{\partial x}{\partial w}\Big/\frac{\partial z}{\partial w} - \frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v}\right)\right] . \qquad \text{(II-C-58)}$$

Solving equation (II-C-58) for P we have

$$P\left[\left(\frac{\partial x}{\partial u}\Big/\frac{\partial z}{\partial u} - \frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v}\right)\left(\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial w}\Big/\frac{\partial z}{\partial w}\right)\right.$$

$$\left. - \left(\frac{\partial x}{\partial w}\Big/\frac{\partial z}{\partial w} - \frac{\partial x}{\partial v}\Big/\frac{\partial z}{\partial v}\right)\left(\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial u}\Big/\frac{\partial z}{\partial u}\right)\right]$$

$$= \left[\left(\Pi\Big/\frac{\partial z}{\partial v} - \Omega\Big/\frac{\partial z}{\partial w}\right)\left(\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial u}\Big/\frac{\partial z}{\partial u}\right)\right.$$

$$\left. - \left(\Pi\Big/\frac{\partial z}{\partial v} - \Theta\Big/\frac{\partial z}{\partial u}\right)\left(\frac{\partial y}{\partial v}\Big/\frac{\partial z}{\partial v} - \frac{\partial y}{\partial w}\Big/\frac{\partial z}{\partial w}\right)\right] . \qquad \text{(II-C-59)}$$

Carrying out the multiplications in equation (II-C-59) we obtain

$$P\Bigg[\left(\frac{\partial x}{} \Big/ \partial z ... \right) \quad \partial z \; - \; \partial x \left(\partial z \right) \partial v \left(\Big/ \partial z \right)$$

$$- \left(\frac{\partial x}{\partial v} \Big/ \partial z\right)(\&/\&) \qquad \partial x \left(/ \partial z \right) \left(z \Big/ \frac{\partial z}{\partial w}\right)$$

$$- \left(\frac{\partial x}{\partial w} \Big/ \text{%w)\2v/ dv)} \; + \; \text{[dw/ dw]\du/ du} \right)$$

$$+ \left(\text{dv I dvj\dv/ dvj} \quad \text{\ dv I dv/\c\$u/ 3u/J} \right.$$

$$= \Bigg[\left(\Pi \Big/ \frac{\partial z}{\partial v}\right)\left(\frac{\partial y}{\partial v} \Big/ \frac{\partial z}{\partial v}\right) - \left(\Pi \Big/ \frac{\partial z}{\partial v}\right)\left(\frac{\partial y}{\partial u} \Big/ \frac{\partial z}{\partial u}\right)$$

$$- \left(\Omega \Big/ \frac{\partial z}{\partial w}\right)\left(\frac{\partial y}{\partial v} \Big/ \frac{\partial z}{\partial v}\right) + \left(\Omega \Big/ \frac{\partial z}{\partial w}\right)\left(\frac{\partial y}{\partial u} \Big/ \frac{\partial z}{\partial u}\right)\Bigg]$$

$$+ \Bigg[\left(\Pi \Big/ \frac{\partial z}{\partial v}\right)\left(\frac{\partial y}{\partial w} \Big/ \frac{\partial z}{\partial w}\right) - \left(\Pi \Big/ \frac{\partial z}{\partial v}\right)\left(\frac{\partial y}{\partial v} \Big/ \frac{\partial z}{\partial v}\right)$$

$$- \left(\Theta \Big/ \frac{\partial z}{\partial u}\right)\left(\frac{\partial y}{\partial w} \Big/ \frac{\partial z}{\partial w}\right) + \left(\Theta \Big/ \frac{\partial z}{\partial u}\right)\left(\frac{\partial y}{\partial v} \Big/ \frac{\partial z}{\partial v}\right)\Bigg] . \qquad \text{(II-C-60)}$$

Equation (II-C-60) can then be rewritten as

$$P\left[\frac{\frac{\partial x}{\partial u}\frac{\partial y}{\partial v}}{\frac{\partial z}{\partial u}\frac{\partial z}{\partial v}} - \frac{\frac{\partial x}{\partial u}\frac{\partial y}{\partial w}}{\frac{\partial z}{\partial u}\frac{\partial z}{\partial w}} - \frac{\frac{\partial x}{\partial v}\frac{\partial y}{\partial v}}{\frac{\partial z}{\partial v}\frac{\partial z}{\partial v}} + \frac{\frac{\partial x}{\partial v}\frac{\partial y}{\partial w}}{\frac{\partial z}{\partial v}\frac{\partial z}{\partial w}}\right.$$

$$\left. - \frac{\frac{\partial x}{\partial w}\frac{\partial y}{\partial v}}{\frac{\partial z}{\partial w}\frac{\partial z}{\partial v}} + \frac{\frac{\partial x}{\partial w}\frac{\partial y}{\partial u}}{\frac{\partial z}{\partial w}\frac{\partial z}{\partial u}} + \frac{\frac{\partial x}{\partial v}\frac{\partial y}{\partial v}}{\frac{\partial z}{\partial v}\frac{\partial z}{\partial v}} - \frac{\frac{\partial x}{\partial v}\frac{\partial y}{\partial u}}{\frac{\partial z}{\partial v}\frac{\partial z}{\partial u}}\right]$$

$$= \left[\frac{Q\frac{\partial y}{\partial v}}{\frac{\partial z}{\partial v}\frac{\partial z}{\partial v}} - \frac{Q\frac{\partial y}{\partial u}}{\frac{\partial z}{\partial v}\frac{\partial z}{\partial u}} - \frac{Q\frac{\partial y}{\partial v}}{\frac{\partial z}{\partial w}\frac{\partial z}{\partial v}} + \frac{Q\frac{\partial y}{\partial u}}{\frac{\partial z}{\partial w}\frac{\partial z}{\partial u}}\right. \qquad \text{(II-C-61)}$$

$$\left. - \frac{Q\frac{\partial z}{\partial v}}{\frac{\partial z}{\partial v}\frac{\partial z}{\partial v}} + \frac{Q\frac{\partial y}{\partial w}}{\frac{\partial z}{\partial v}\frac{\partial z}{\partial w}} + \frac{Q\frac{\partial y}{\partial v}}{\frac{\partial z}{\partial u}\frac{\partial z}{\partial v}} - \frac{Q\frac{\partial y}{\partial w}}{\frac{\partial z}{\partial u}\frac{\partial z}{\partial w}}\right].$$

The third term in the bracket in the left side of equation **(II-C-61)** cancels the seventh term in this bracket and the first term in the bracket in the right side of equation **(II-C-61)** cancels the fifth term in this bracket. Multiplying the remaining terms in both sides of equation (II-C-61) by

$\left(\frac{\partial z}{\partial u}\,\frac{\partial z}{\partial v}\,\frac{\partial z}{\partial w}\right)$ we obtain

$$P\left[\frac{\partial x}{\partial u}\frac{\partial y}{\partial v}\frac{\partial z}{\partial w} - \frac{\partial x}{\partial u}\frac{\partial y}{\partial w}\frac{\partial z}{\partial v} + \frac{\partial x}{\partial v}\frac{\partial y}{\partial w}\frac{\partial z}{\partial u} - \frac{\partial x}{\partial w}\frac{\partial y}{\partial v}\frac{\partial z}{\partial u} + \frac{\partial x}{\partial w}\frac{\partial y}{\partial u}\frac{\partial z}{\partial v} - \frac{\partial x}{\partial v}\frac{\partial y}{\partial u}\frac{\partial z}{\partial w}\right]$$

$$= \Theta\left[\ \ \partial u \ \ \partial v \qquad \partial v \ \ \partial u \qquad \partial u \ \ \partial v\ \ \right] \qquad \text{(II-C-62)}$$

$$+ \Pi\left[\ \ \partial w \ \ \partial u \qquad \partial v \ \ \partial w \qquad \partial w \ \ \partial v\ \ \right]$$

Now P(x, y, z) is the total derivative of Γ along a line parallel to the x-axis in (x, y, z)-space. Also Θ(u, v, w) is the total derivative of Γ along a line parallel to the u-axis in (u, v, w)-space, Π(u, v, w) is the total derivative of Γ along a line parallel to the v-axis in (u, v, w)-space, and Ω(u, v, w) is the total derivative of Γ along a line parallel to the w-axis in (u, v, w)-space. Thus we have from equation (II-C-62)

$$P(x, y, z) = \left(\frac{\partial \Gamma}{\partial x}\right)_{y,z} = \frac{\begin{vmatrix} \frac{\partial \Gamma}{\partial u} & \frac{\partial \Gamma}{\partial v} & \frac{\partial \Gamma}{\partial w} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \\ \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \end{vmatrix}}{\begin{vmatrix} \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} & \frac{\partial x}{\partial w} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \\ \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \end{vmatrix}}. \qquad \text{(II-C-63)}$$

Likewise $Q(x, y, z)$ is the total derivative of T along a line parallel to the y-axis in (x, y, z)-space. Thus in a similar way we have

$$Q(x,y,z) = \left(\frac{\partial T}{\partial y}\right)_{x,z} = \frac{\begin{vmatrix} \frac{\partial T}{\partial u} & \frac{\partial T}{\partial v} & \frac{\partial T}{\partial w} \\ \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} & \frac{\partial x}{\partial w} \\ \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \end{vmatrix}}{\begin{vmatrix} \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \\ \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} & \frac{\partial x}{\partial w} \\ \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \end{vmatrix}} . \qquad \text{(II-C-64)}$$

Also $R(x, y, z)$ is the total derivative of T along a line parallel to the z-axis in (x, y, z)-space. Consequently in a similar way we have finally

$$R(x,y,z) = \left(\frac{\partial T}{\partial z}\right)_{x,y} = \frac{\begin{vmatrix} \frac{\partial T}{\partial u} & \frac{\partial T}{\partial v} & \frac{\partial T}{\partial w} \\ \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} & \frac{\partial x}{\partial w} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \end{vmatrix}}{\begin{vmatrix} \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \\ \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} & \frac{\partial x}{\partial w} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \end{vmatrix}} . \qquad \text{(II-C-65)}$$

Appendix D to Part II

Discussion of F.G. Donnan's derivation of the equation $du = tds - pdv + \mu dm$ for a one-component system of one phase and of variable mass

Donnan's[1] proof of the equation

$$du = tds - pdv + \mu dm$$

for a one-component system of one phase and of variable mass is as follows:

> Applied to a homogeneous system characterized by a uniform temperature t and a uniform pressure p, and subject to no other external forces except that due to this pressure, the development of thermodynamics up to the date of Gibbs' researches may perhaps be briefly summarized in the equation of Clausius, $\delta u = t\delta s - p\delta v$, where u = energy, s = entropy, and v = volume. This equation applies to a closed system of *constant* total mass, and the first fundamental step taken by Gibbs was to extend it to a system of *variable* mass. In the equation of Clausius the entropy of the system may be changed by the addition or subtraction of heat, whilst the volume may be altered by work done by or on the system, both types of change producing corresponding changes in the energy. It is possible, however, simultaneously to increase or diminish the energy, entropy, and volume of the system by increasing or diminishing its mass, whilst its internal physical state, as determined by its temperature and pressure, remains the same. If we are dealing with a system whose energy, entropy and

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[1] Donnan, F.G., *The Influence of J. Willard Gibbs on the Science of Physical Chemistry, An Address on the Occasion of the Centenary Celebration of the Founding of the Franklin Institute,* Philadelphia, The Franklin Institute, 1924, pp. 6, 7.

volume may be regarded as sensibly proportional, at constant temperature and pressure, to its mass, we may write:

$$du = 6u + u_0 dm$$

$$ds = 6s + s_0 dm$$

$$dv = Sv + v_o dm$$

where the total differentials du, ds_9 and *dv* indicate changes which take account of variation of mass at constant temperature and pressure as well as of heat and work effects at constant mass (indicated by the differentials 6u, 6s, *5v*) and u_o» *SQ,* v_{Qf} denote the energy, entropy, and volume, respectively, of unit mass under the specified conditions of temperature and pressure. Combining these equations with that of Clausius, we obtain

$$du = tds - pdv + (u_0 - ts_Q + pv_Q)dm$$

or, putting

$$u_0 - ts_0 + pvo = li$$

$$du = tds - pdv + udoi.$$

According to Donnan the total differentials du_f *ds,* and *dv* indicate the changes in *u* s,* and *v* which take account of variation of mass at constant temperature and constant pressure as well as of heat and **work** effects at constant mass. In **Donnan's** equation $du = 8u + uodm$ the term u^dm_9 *UQ* being the specific energy, gives the change in energy with mass at constant temperature and constant pressure; it does not give the change in energy with nass at constant entropy and constant volume. The independent variables in the right side of this equation are thus temperature, pressure, and mass. The differential δu is consequently really shorthand for $\frac{\partial u}{\partial t}dt + \frac{\partial u}{\partial p}dp$. Likewise in the equation $ds = \delta s + s_0 dm$, where s_0 is the specific entropy, the term δs is really shorthand for $\frac{\partial s}{\partial t}dt + \frac{\partial s}{\partial p}dp$. Similarly in the equation $dv = \delta v + v_0 dm$, where v_0 is the specific volume, the term δv is really shorthand for $\frac{\partial v}{\partial t}dt + \frac{\partial v}{\partial p}dp$. Thus written out in full we have

$$du = \frac{\partial u}{\partial t}dt + \frac{\partial u}{\partial p}dp + u_0 dm \, , \qquad \text{(II-D-1)}$$

$$ds = \frac{\partial s}{\partial t}dt + \frac{\partial s}{\partial p}dp + s_0 dm \, , \qquad \text{(II-D-2)}$$

and

$$dv = \frac{\partial v}{\partial t}dt + \frac{\partial v}{\partial p}dp + v_0 dm \, . \qquad \text{(II-D-3)}$$

Combining equations (II-D-1), (II-D-2) and (II-D-3) we have

$$du - t\,ds + p\,dv$$

$$= \frac{\partial u}{\partial t}dt + \frac{\partial u}{\partial p}dp - t\frac{\partial s}{\partial t}dt - t\frac{\partial s}{\partial p}dp + p\frac{\partial v}{\partial t}dt + p\frac{\partial v}{\partial p}dp$$

$$+ (u_0 - ts_0 + pv_0)dm \, . \qquad \text{(II-D-4)}$$

It is known from the case of a one-component system of one phase and constant mass that

$$\frac{\partial u}{\partial t} = m\left(\breve{c}_p - p\frac{\partial \breve{v}}{\partial t}\right), \qquad \text{(II-D-5)}$$

$$\frac{\partial u}{\partial p} = m\left(\breve{l}_p - p\frac{\partial \breve{v}}{\partial p}\right). \qquad \text{(II-D-6)}$$

$$\frac{\partial s}{\partial t} = m\frac{\breve{c}_p}{t}, \qquad \text{(II-D-7)}$$

$$\frac{\partial s}{\partial p} = m\frac{\breve{l}_p}{t}, \qquad \text{(II-D-8)}$$

$$\frac{\partial v}{\partial t} = m\frac{\partial \breve{v}}{\partial t}, \qquad \text{(II-D-9)}$$

and

$$\frac{\partial v}{\partial p} = m\frac{\partial \breve{v}}{\partial p}. \qquad \text{(II-D-10)}$$

Substituting these values of the partial derivatives of u and s from equations (II-D-5), (II-D-6), (II-D-7), (II-D-8), (II-P-9), and (II-D-10), in equation (II-D-4) we obtain

$$\begin{aligned} du - tds + pdv &= m\left(\breve{c}_p - p\frac{\partial \breve{v}}{\partial t}\right)dt + m\left(\breve{l}_p - p\frac{\partial \breve{v}}{\partial p}\right)dp - mt\frac{\breve{c}_p}{t}dt \\ &\quad - mt\frac{\breve{l}_p}{t}dp + mp\frac{\partial \breve{v}}{\partial t}dt + mp\frac{\partial \breve{v}}{\partial p}dp + (u_0 - ts_0 + pv_0)dm. \end{aligned} \qquad \text{(II-D-11)}$$

Thus we arrive at Donnan's equation

$$du = t\,ds - p\,dv + (u_0 - ts_0 + pv_0)\,dm\,, \qquad \text{(II-D-12)}$$

but by this mode of derivation the independent variables are still t, p, and m, not s, v, and m.

The real problem Donnan was attempting to solve was to show that when the independent variables in the case of a one-component system of one phase and of variable mass are entropy, volume, and mass, the partial derivatives of the energy are $\frac{\partial u}{\partial s} = t$, $\frac{\partial u}{\partial v} = -p$, and $\frac{\partial u}{\partial m} = (u_0 - ts_0 + pv_0)$. In order to solve this problem Donnan had to begin with temperature, pressure, and mass as independent variables, because the change of energy with mass is only equal to the specific energy at constant temperature and constant pressure. The real problem then consists in a transformation from temperature, pressure, and mass as independent variables to entropy, volume, and mass as independent variables.

It is assumed that the equations

$$s = F(t,p,m) \qquad \text{(II-D-13)}$$

and

$$v = \phi(t,p,m) \qquad \text{(II-D-14)}$$

can be solved so that we have

$$t = F(s, v, m) \qquad \text{(II-D-15)}$$

and

$$p = \phi(s, v, m) \qquad \text{(II-D-16)}$$

and thus finally

$$u = V(s, v, m) \; . \qquad \text{(II-D-17)}$$

From equation (II-D-17) it follows that

$$du = \frac{\partial u}{\partial s} ds + \frac{\partial u}{\partial v} dv + \frac{\partial u}{\partial m} dm \; . \qquad \text{(II-D-18)}$$

The partial derivatives $\frac{\partial u}{\partial s}$, $\frac{\partial u}{\partial v}$, and $\frac{\partial u}{\partial m}$ are then obtainable by the use of the Jacobians in Tables (II-D-10), (II-D-12), and (II-D-14). Thus we have

$$\left(\frac{\partial u}{\partial s}\right)_{m,v} = \frac{\dfrac{\partial(u, m, v)}{\partial(t, p, m)}}{\dfrac{\partial(s, m, v)}{\partial(t, p, m)}} = \frac{-m^2\left\{t\left(\dfrac{\partial \breve{v}}{\partial t}\right)^2_{p,m} + \breve{c}_p\left(\dfrac{\partial \breve{v}}{\partial p}\right)_{t,m}\right\}}{-m^2\left\{\left(\dfrac{\partial \breve{v}}{\partial t}\right)^2_{p,m} + \dfrac{\breve{c}_p}{t}\left(\dfrac{\partial \breve{v}}{\partial p}\right)_{t,m}\right\}}$$

$$= t \; , \qquad \text{(II-D-19)}$$

$$\left(\frac{\partial u}{\partial v}\right)_{m,s} = \frac{\dfrac{\partial(u, m, s)}{\partial(t, p, m)}}{\dfrac{\partial(v, m, s)}{\partial(t, p, m)}} = \frac{-m^2\left\{p\left(\dfrac{\partial \breve{v}}{\partial t}\right)^2_{p,m} + \dfrac{p\breve{c}_p}{t}\left(\dfrac{\partial \breve{v}}{\partial p}\right)_{t,m}\right\}}{m^2\left\{\left(\dfrac{\partial \breve{v}}{\partial t}\right)^2_{p,m} + \dfrac{\breve{c}_p}{t}\left(\dfrac{\partial \breve{v}}{\partial p}\right)_{t,m}\right\}}$$

= . ·U)

and

$$\left(\frac{\partial u}{\partial m}\right)_{v,s} = \frac{\dfrac{\partial(u, v, s)}{\partial(t, p, m)}}{\dfrac{\partial(m, v, s)}{\partial(t, p, m)}}$$

$$= \frac{-m^2\left\{\left[\dfrac{\breve{c}_p}{t}\left(\dfrac{\partial \breve{v}}{\partial p}\right)_{t,m} + \left(\dfrac{\partial \breve{v}}{\partial t}\right)^2_{p,m}\right](u_0 + pv_0 - ts_0)\right\}}{-m^2\left\{\dfrac{\breve{c}_p}{t}\left(\dfrac{\partial \breve{v}}{\partial p}\right)_{t,m} + \left(\dfrac{\partial \breve{v}}{\partial t}\right)^2_{p,m}\right\}}$$

$$= u_0 + pv_0 - ts_0 \ . \qquad \text{(II-D-21)}$$

In the case of a one-component system of one phase and of variable mass the chemical potential μ is equal to $\left(\frac{\partial u}{\partial m}\right)_{v,s}$ and consequently to $(u_0 + pv_0 - ts_0)$. Substituting the values of $\left(\frac{\partial u}{\partial s}\right)_{m,v}$, $\left(\frac{\partial u}{\partial v}\right)_{m,s}$, and $\left(\frac{\partial u}{\partial m}\right)_{v,s}$ from equations (II-D-19), (II-D-20), and (II-D-21) in equation (II-D-18) we arrive at the result

$$du = t\,ds - p\,dv + \mu\,dm \ , \qquad \text{(II-D-22)}$$

with s, v, and m as independent variables. Equation (II-D-22) is thus true with either t, p, and m as independent variables or with s, v, and m as independent variables. However, the more important significance of equation (II-D-22) is that it is true with s, v, and m as Independent variables.

Part III

Relations between thermodynamic quantities and their first derivatives in a binary system of one phase and of unit mass

'Introduction

The basic thermodynamic relations for systems of variable composition were first derived by J. Willard Gibbs in his memoir entitled "On the Equilibrium of Heterogeneous Substances."[1] Gibbs[2] stated that the nature of the equations which express the relations between the energy, entropy, volume, and the quantities of the various components for homogeneous combinations of the substances in the given mass must be found by experiment. The manner in which the experimental determinations are to be carried out was indicated by him[3] in the following words: ffAs, however, it is only differences of energy and of entropy that can be measured, or indeed that have a physical meaning, the values of these quantities are so far arbitrary, that we may choose independently for each simple substance the state in which its energy and its entropy are both zero. The values of the

[1] Gibbs, J. Willard, Trans. Conn, Acad. of Arts and Sciences, 3, 108-248, 1874-78, or *Collected Works,* Longmans, Green and Company, New York, 1928, Vol. 1, pp. 55-184.

[2] Gibbs, J. Willard, Trans. Conn. Acad. of Arts and Sciences, 3, 140, 1874-78, or *Collected Works*, Longmans, Green and Company, New York, 1928, Vol. 1, p. 85.

[3] Gibbs, J. Willard, Trans. Conn. Acad. of Arts and Sciences, 3, 140-141, 1874-78, or *Collected Works,* Longmans, Green and Company, New York, 1928, Vol. 1, p. 85.

energy and the entropy of any compound body in any particular state will then be fixed. Its energy will be the sum of the work and heat expended in bringing its components from the states in which their energies and their entropies are zero into combination and to the state in question; and its entropy is the value of the integral $\int \frac{dQ}{t}$ for any reversible process by which that change is effected (dQ denoting an element of the heat communicated to the matter thus treated, and t the temperature of the matter receiving it)."

Calculation of the specific volume, the specific energy, and the specific entropy of a binary system of one phase as functions of the absolute thermodynamic temperature, the pressure, and the mass fraction of one component from experimental measurements[4]

In the case of a binary system of one phase, the mass fraction $\breve{m}_1$ of component 1 is defined by the equation

$$\breve{m}_1 \equiv \frac{m_1}{m_1 + m_2} , \qquad \text{(III-1)}$$

where m_1 denotes the mass of component 1 and m_2 denotes the

[4] Tunell, G., *Relations between Intensive Thernodynamic Quantities and Their First Derivatives in a Binary System of* 9nt> *Phase,* V.H. Freeman and Co., San Francisco and" London, *I9ti\ pr).* 7-16.

mass of component 2; the specific volume $\breve{V}$ is defined by the equation

$$\breve{V} \equiv \frac{V}{m_1 + m_2} \quad , \qquad \text{(III-2)}$$

where V denotes the total volume; the specific energy $\breve{U}$ *is* defined by the equation

$$\breve{U} = \frac{U}{mi + m_2} \quad , \qquad \text{(III-3)}$$

v/here £/ denotes the total energy; the specific entropy $\breve{S}$ is defined by the equation

$$\breve{S} \equiv \frac{S}{\cdot mi + m_2} \quad , \qquad \text{(III-4)}$$

v/here S denotes the total entropy. As a result of experiment it is known that the pressure p_9 the specific volume $\breve{V}_f$ the absolute thermodynamic temperature T, and the mass fraction *Si* of component 1 are connected by an equation of state

$$*(p_f \breve{V} * 7\backslash \breve{m}_1) = 0 \; , \qquad \text{(111-5)}$$

which can, in general, be solved for any one of these quantities as a function of the other three. The relation of the specific energy of such a system to the temperature, pressure, and sass fraction of component 1 is expressed by the equation

$$= \int_{T_0,\, p_0,\, \breve{m}_{1_0}}^{T,\, p,\, \breve{m}_1} \left\{ \left[\breve{c}_p - p\frac{\partial \breve{V}}{\partial T} \right] dT + \left[\breve{l}_p - p\frac{\partial \breve{V}}{\partial p} \right] dp + \frac{\partial \breve{V}}{\partial \breve{m}_1} d\breve{m}_1 \right\}, \qquad \text{(III-6)}$$

where $\breve{c}_p$ denotes the heat capacity at constant pressure per unit of mass and $\breve{l}_p$ denotes the latent heat of change of pressure at constant temperature per unit of mass. The relation of the specific entropy $\breve{S}$ to the temperature, pressure, and mass fraction of component 1 is expressed by the equation

$$\breve{S}(T, p, \breve{m}_1) - \breve{S}(T_0, p_0, \breve{m}_{1_0})$$

$$= \int_{T_0,\, p_0,\, \breve{m}_{1_0}}^{T,\, p,\, \breve{m}_1} \left\{ \frac{\breve{c}_p}{T} dT + \frac{\breve{l}_p}{T} dp + \frac{\partial \breve{S}}{\partial \breve{m}_1} d\breve{m}_1 \right\}. \qquad \text{(III-7)}$$

Necessary and sufficient conditions[5] for (III-6) are

$$\left\{ \frac{\partial \left[\breve{l}_p - p\frac{\partial \breve{V}}{\partial p} \right]}{\partial T} \right\}_{p,\, \breve{m}_1} = \left\{ \frac{\partial \left[\breve{c}_p - p\frac{\partial \breve{V}}{\partial T} \right]}{\partial p} \right\}_{T,\, \breve{m}_1}, \qquad \text{(III-8)}$$

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5 Osgood, W.F., *Advanced Calculus*, The Macmillan Company, New York, 1925, p. 232, and *Lehrbuch der Funktionentheorie*, Bd. 1, 5te Aufl., B.G. Teubner, Leipzig, 1928, pp. 142-150.

$$\left\{ \frac{\partial \left(\frac{\partial \breve{U}}{\partial \breve{m}_1} \right)_{T,p}}{\partial T} \right\}_{p,\, \breve{m}_1} = \left\{ \frac{\partial \left[\breve{c}_p - p \left(\frac{\partial \breve{V}}{\partial T} \right)_{p,\, \breve{m}_1} \right]}{\partial \breve{m}_1} \right\}_{T,\, p} , \qquad \text{(III-9)}$$

and

$$\left\{ \frac{\partial \left(\frac{\partial \breve{U}}{\partial \breve{m}_1} \right)_{T,p}}{\partial p} \right\}_{T,\, \breve{m}_1} = \left\{ \frac{\partial \left[\breve{l}_p - p \left(\frac{\partial \breve{V}}{\partial p} \right)_{T,\, \breve{m}_1} \right]}{\partial \breve{m}_1} \right\}_{T,\, p} . \qquad \text{(III-10)}$$

Similarly, necessary and sufficient conditions for (III-7) are

$$\left\{ \frac{\partial \frac{\breve{l}_p}{T}}{\partial T} \right\}_{p,\, \breve{m}_1} = \left\{ \frac{\partial \frac{\breve{c}_p}{T}}{\partial p} \right\}_{T,\, \breve{m}_1} , \qquad \text{(III-11)}$$

$$\left\{ \frac{\partial \left(\frac{\partial \breve{S}}{\partial \breve{m}_1} \right)_{T,p}}{\partial T} \right\}_{p,\, \breve{m}_1} = \left\{ \frac{\partial \frac{\breve{c}_p}{T}}{\partial \breve{m}_1} \right\}_{T,\, p} , \qquad \text{(III-12)}$$

and

$$\left\{ \frac{\partial \left(\frac{\partial \breve{S}}{\partial \breve{m}_1} \right)_{T,p}}{\partial p} \right\}_{T,\, \breve{m}_1} = \left\{ \frac{\partial \frac{\breve{l}_p}{T}}{\partial \breve{m}_1} \right\}_{T,\, p} . \qquad \text{(III-13)}$$

Carrying out the indicated differentiations in (III-8) and

(III–11) one obtains

$$\frac{\partial \breve{l}_p}{\partial T} - p\frac{\partial^2 \breve{V}}{\partial T \partial p} = \frac{\partial \breve{c}_p}{\partial p} - p\frac{\partial^2 \breve{V}}{\partial p \partial T} - \frac{\partial \breve{V}}{\partial T} \qquad \text{(III-14)}$$

and

$$\frac{1}{T}\frac{\partial \breve{l}_p}{\partial T} - \frac{\breve{l}_p}{T^2} = \frac{1}{T}\frac{\partial \breve{c}_p}{\partial p} . \qquad \text{(III-15)}$$

Combining (III-14) and (III-15) one has

$$\breve{l}_p = -T\frac{\partial \breve{V}}{\partial T} . \qquad \text{(III-16)}$$

Carrying out the indicated differentiations in (III-9) and (III-12) one obtains

$$\frac{\partial^2 \breve{U}}{\partial T \partial \breve{m}_1} = \frac{\partial \breve{c}_p}{\partial \breve{m}_1} - p\frac{\partial^2 \breve{V}}{\partial \breve{m}_1 \partial T} \qquad \text{(III-17)}$$

and

$$\frac{\partial^2 \breve{S}}{\partial T \partial \breve{m}_1} = \frac{1}{T}\frac{\partial \breve{c}_p}{\partial \breve{m}_1} . \qquad \text{(III-18)}$$

Combining (III-17) and (III-18) one has

$$\frac{\partial^2 \breve{U}}{\partial T \partial \breve{m}_1} = T\frac{\partial^2 \breve{S}}{\partial T \partial \breve{m}_1} - p\frac{\partial^2 \breve{V}}{\partial \breve{m}_1 \partial T} . \qquad \text{(III-19)}$$

Carrying out the indicated differentiations in (111-10) and (111-13) one obtains

$$\frac{\partial^2 \breve{U}}{\partial p\,\partial \breve{m}_1} = \frac{\partial \breve{l}_p}{\partial T} - p\,\frac{\partial^2 \breve{V}}{\partial p\,\partial T} \qquad \text{(III-20)}$$

and

$$\frac{\partial^2 \breve{S}}{\partial p\,\partial \breve{m}_1} = \frac{1}{T}\,\frac{\partial \breve{l}}{\partial p}\,. \qquad \text{(111-21)}$$

Combining (111-20) and (111-21) one has

$$\frac{\partial^2 \breve{U}}{\partial p\,\partial \breve{m}_1} = T\,\frac{\partial^2 \breve{S}}{\partial p\,\partial \breve{m}_1} - p\,\frac{\quad}{\partial \breve{m}_1\,\partial p}\,. \qquad \text{(III-22)}$$

From (111-16) it follows that

$$\frac{\partial \breve{l}_p}{\partial T} = - \frac{\partial^2 \breve{\ }}{[illegible]} - \frac{\partial \breve{V}}{\partial T} \qquad \text{(III-23)}$$

and from (111-14) and (111-16) one obtains

$$\frac{\partial \breve{C}_p}{\partial p} = -T\,\frac{\partial^2 \breve{V}}{\partial T^2}\,. \qquad \text{(III-24)}$$

From (111-16) it also follows that

$$\frac{\partial \breve{\ }}{\partial p} = -T\,\frac{\partial^2 \breve{V}}{\partial p\,\partial T} \qquad \text{(III-25)}$$

and

$$\frac{\partial \breve{C}_p}{\partial \breve{m}_1} = -T \frac{\partial^2 \breve{V}}{\partial \breve{m}_1 \partial T} . \qquad \text{(III-26)}$$

Combining (III-26) and (III-20) one has

$$\frac{\partial^2 U}{\partial p \partial \breve{m}_1} = -T \frac{\partial^2 V}{\partial \breve{m}_1 \partial T} - p \frac{\partial^2 V}{\partial \breve{m}_1 \partial p} , \qquad \text{(III-27)}$$

and, similarly, combining (III-26) and (III-21) one has

$$\frac{\partial^2 \breve{S}}{\partial p \partial \breve{m}_1} = -\frac{\partial^2 \breve{V}}{\partial \breve{m}_1 \partial T} . \qquad \text{(III-28)}$$

There is thus one relation, equation (III-16), between the seven quantities $\frac{\partial \breve{V}}{\partial T}$, $\frac{\partial \breve{V}}{\partial p}$, $\frac{\partial \breve{V}}{\partial \breve{m}_1}$, $\breve{c}_p$, $\breve{C}_p$, $\frac{\partial \breve{U}}{\partial \breve{m}_1}$, $\frac{\partial \breve{S}}{\partial \breve{m}_1}$. Consequently, all seven will be known if the following six are determined by means of experimental measurements: $\frac{\partial \breve{V}}{\partial T}$, $\frac{\partial \breve{V}}{\partial p}$, $\frac{\partial \breve{V}}{\partial \breve{m}_1}$, $\breve{c}_p$, $\frac{\partial \breve{U}}{\partial \breve{m}_1}$, $\frac{\partial \breve{S}}{\partial \breve{m}_1}$.

There are also eight relations, equations (III-17), (III-18), (III-23), (III-24), (III-25), (III-26), (III-27), (III-28), between the eighteen quantities, $\frac{\partial^2 \breve{V}}{\partial T^2}$, $\frac{\partial^2 \breve{V}}{\partial p^2}$, $\frac{\partial^2 \breve{V}}{\partial \breve{m}_1^2}$, $\frac{\partial^2 \breve{V}}{\partial T \partial p}$, $\frac{\partial^2 \breve{V}}{\partial T \partial \breve{m}_1}$, $\frac{\partial^2 \breve{V}}{\partial p \partial \breve{m}_1}$, $\frac{\partial c_p}{\partial T}$, $\frac{\partial c_p}{\partial p}$, $\frac{\partial c_p}{\partial \breve{m}_1}$, $\frac{\partial \breve{C}_p}{\partial T}$, $\frac{\partial \breve{C}_p}{\partial p}$, $\frac{\partial \breve{C}_p}{\partial \breve{m}_1}$, $\frac{\partial^2 \breve{U}}{\partial T \partial \breve{m}_1}$, $\frac{\partial^2 \breve{U}}{\partial p \partial \breve{m}_1}$, $\frac{\partial^2 \breve{U}}{\partial \breve{m}_1^2}$, $\frac{\partial^2 \breve{S}}{\partial T \partial \breve{m}_1}$, $\frac{\partial^2 \breve{S}}{\partial p \partial \breve{m}_1}$, $\frac{\partial^2 \breve{S}}{\partial \breve{m}_1^2}$, by means of which from the following ten, $\frac{\partial \breve{V}}{\partial T}$, $\frac{\partial \breve{V}}{\partial p}$, $\frac{\partial \breve{V}}{\partial \breve{m}_1}$, $\frac{\partial^2 \breve{V}}{\partial T \partial p}$, $\frac{\partial^2 \breve{V}}{\partial T \partial \breve{m}_1}$, $\frac{\partial^2 \breve{V}}{\partial p \partial \breve{m}_1}$, $\frac{\partial \breve{Z}_p}{\partial T}$, $\frac{\partial \breve{C}_p}{\partial \breve{m}_1}$, $\frac{\partial^2 \breve{U}}{\partial T \partial \breve{m}_1}$, $\frac{\partial^2 \breve{S}}{\partial T \partial \breve{m}_1}$, the remaining eight can be calculated. From equation (III-24) $\frac{\partial \breve{C}_p}{\partial p}$ can be calculated; from equation (III-23) $\frac{\partial \breve{l}_p}{\partial T}$ can be calculated; from equation (III-25) $\frac{\partial \breve{l}_p}{\partial \breve{m}_1}$ can be calculated; from equation (III-26) $\frac{\partial \breve{l}_T}{\partial \breve{m}_1}$ can be calculated; from equation (III-17) $\frac{\partial^2 \breve{U}}{\partial T \partial \breve{m}_1}$ can be calculated; from equation (III-27) $\frac{\partial^2 \breve{U}}{\partial p \partial \breve{m}_1}$ can be calculated; from equation (III-18) $\frac{\partial^2 \breve{S}}{\partial T \partial \breve{m}_1}$ can be calculated; and from equation (III-28) $\frac{\partial^2 \breve{S}}{\partial p \partial \breve{m}_1}$ can be calculated. It will therefore suffice to determine experimentally $\frac{\partial \breve{V}}{\partial \breve{m}_1}$ along a line at constant temperature, T', and constant pressure, p', then to determine experimentally $\frac{\partial \breve{V}}{\partial T}$ at all points in a plane at constant pressure, p', and $\frac{\partial \breve{V}}{\partial p}$ at all points in $(T, p, \breve{m}_1)$-space, likewise to determine $\breve{C}_p$ at all points in a plane at constant pressure, p', and to determine experimentally $\frac{\partial \breve{U}}{\partial \breve{m}_1}$ along a line at constant temperature, T', and constant pressure, p', and also $\frac{\partial \breve{S}}{\partial \breve{m}_1}$ along a line at constant temperature, T', and constant pressure, p'.

From measurements of specific volumes over the range of temperature, pressure, and composition that is of interest, the values of $\frac{\partial V}{\partial T}$, $\frac{\partial V}{\partial p}$ and $\frac{\partial V}{\partial m_1}$ can be obtained. By means of calorimetric measurements the necessary values of $\bar{c}_p$ can also be obtained. The determination of 9/7 rj- offli at constant temperature and pressure over the range of composition of interest can be accomplished in many cases by means of a constant volume calorimeter, and in some cases dlJ -^p- can be determined by means of measurements of the electromotive force of a galvanic ceil at constant pressure over the ranges of composition and temperature of interest in combination with the measurements of specific volume. The determination of -rzr- dmi at constant temperature and pressure over the range of composition of interest can be accomplished most readily by measurements of the electromotive force of a galvanic cell at constant temperature and pressure if a suitable cell is available.

The methods of determination of -re- dini and -^r- dmi by means of electromotive force Measurements can be illustrated by the following example. In the case of a galvanic cell consisting of electrodes which are liquid thallium amalgams of different concentrations both immersed in the same solution of a thallium salt, one has

$$\bar{G}_2 - \bar{G}_2' = -NF\mathcal{E}, \qquad (111\text{-}29)$$[6]

where G denotes the Gibbs function, $U + pV - TS$, of a liquid thallium amalgam, $\bar{G}_2$ denotes the partial derivative $\left(\frac{\partial G}{\partial n_2}\right)_{T,p,n_1}$ at the concentration of one electrode, $\bar{G}_2'$ the same partial derivative at the concentration of the other electrode, n_2 the number of gram atoms of thallium, n_1 the number of gram atoms of mercury, N the number of Faradays the passage of which through the cell accompanies the reversible transfer of one gram atom of thallium from the one amalgam to the other (N = 1 in this case since a pure thallous salt was used as the electrolyte), F the Faraday equivalent (which is equal to the charge of one electron times the number of atoms in a gram atom); and $\mathcal{E}$ the electromotive force. The values of the electromotive forces of a number of such cells, including one in which one electrode was a saturated liquid thallium amalgam, were determined at 20°C and 1 atmosphere by Richards and Daniels.[7] By measurement of the electromotive force of another galvanic cell in which the electrodes are finely divided pure crystalline thallium and thallium saturated liquid amalgam at the same temperature and pressure, the

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[6] Lewis, G. M.» and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances** McGraw-Hill Book Company, Inc., Mew York, 1923,. p. 265.

[7] Richards, T. W,, and F. .Daniels, Jour. Amer. Chen. Soc., 41, 1732-1768, 1919.

difference $\bar{G}_2^s - G_2$ could be evaluated, $\bar{G}_2^s$ denoting the value of $\bar{G}_2$ in the saturated liquid thallium amalgam, and G_2 the value of the function G for pure crystalline thallium per gram atom.[8] The value of G_2 being assumed known from measurements on pure thallium, the values of $\bar{G}_2$ in liquid amalgams of different concentrations are then obtainable from the measurements of electromotive force in the two kinds of cell. From the values of $\bar{G}_2$, the values of $\bar{G}_1 - G_1$ are calculable by the use of the equation

$$\bar{G}_1 - G_1 = -\int_0^{\hat{n}_2} \frac{\hat{n}_2}{\hat{n}_1} \frac{d\bar{G}_2}{d\hat{n}_2}\, d\hat{n}_2 \text{ ,[9]} \qquad \text{(III-30)}$$

where $\hat{n}_2$ denotes the gram atom fraction of thallium in the amalgams,

$$\hat{n}_2 \equiv \frac{n_2}{n_1 + n_2} \text{ ,} \qquad \text{(III-31)}$$

and $\hat{n}_1$ the gram atom fraction of mercury,

$$\hat{n}_1 \equiv \frac{n_1}{n_1 + n_2} \text{ ,} \qquad \text{(III-32)}$$

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[8] Richards, T.W., and F. Daniels, op. cit., pp. 1732-1768; Lewis, G.N., and M. Randall, op. cit., pp. 413-414.

[9] Lewis, G.N., and M. Randall, op. cit., p. 44; cf. also Gibbs, J. Willard, Trans. Conn. Acad. of Arts and Sciences, 3, 194, 1874-78, or *Collected Works,* Longmans, Green and Company, New York, 1925, Vol. 1, p. 135.

$\bar{G}_1$ the partial derivative $\left(\frac{\partial G}{\partial n_1}\right)_{T, p, n_2}$, and G_1^* the value of the function G for pure mercury per gram atom. The integrand in the integral on the right side of equation (III-30) remains finite and approaches a limit as x_2 approaches zero and the value of the integral is thus determinable.[10] The value of G_1 is assumed to be known from

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[10] Gibbs showed that in the case of a solution in which the mass of the substance chosen as the solute is capable of negative values, the quantity $m_2\left(\frac{\partial \mu_2}{\partial m_2}\right)_{T, p, m_1}$ approaches zero as a limit when m_2 approaches zero, T, p, and m_1 being held constant, μ_2 denoting the derivative $\left(\frac{\partial \zeta}{\partial m_2}\right)_{T, p, m_1}$; he also showed that in the case of a solution in which the mass of the substance chosen as the solute is incapable of negative values, as is true of thallium amalgams, the quantity $m_2\left(\frac{\partial \mu_2}{\partial m_2}\right)_{T, p, m_1}$ still remains finite, and it approaches a limit greater than zero when m_2 approaches zero, T, p, and m_1 being held constant, even though the derivative $\left(\frac{\partial \mu_2}{\partial m_2}\right)_{T, p, m_1}$ becomes infinite in this case (Gibbs, J. Willard, Trans. Conn. Acad. of Arts and Sciences, 3, 194-196, 1874-78, or *Collected Works,* Longmans, Green and Company, New York, 1928, Vol. 1, pp. 135-137). It follows in the same way that the quantity $n_2\left(\frac{\partial \bar{G}_2}{\partial n_2}\right)_{T, p, n_1}$ also approaches a limit when n_2 approaches zero, T, p, and n_1 being held constant. By application of the change of variable theorem in partial

measurements on pure mercury, and hence $\bar{G}_1$ can be obtained as a function of the gram atom fraction at 20°C and 1 atmosphere. The derivative $\left(\frac{\partial G}{\partial m_2}\right)_{T, p, m_1}$ can be calculated from the equation

$$\left(\frac{\partial G}{\partial m_2}\right)_{T, p, m_1} = \frac{\bar{G}_2}{A_2} , \qquad \text{(III-33)}$$

where A_2 denotes the number of grams in a gram atom of thallium, and the derivative $\left(\frac{\partial G}{\partial m_1}\right)_{T, p, m_2}$ can be calculated

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differentiation one obtains the relation

$$\left(\frac{\partial \bar{G}_2}{\partial n_2}\right)_{T, p, n_1} = \left(\frac{\partial \bar{G}_2}{\partial \hat{n}_2}\right)_{T, p} \frac{n_1}{(n_1 + n_2)^2} .$$

Multiplying both sides of this equation by n_2, one has

$$n_2\left(\frac{\partial \bar{G}_2}{\partial n_2}\right)_{T, p, n_1} = \left(\frac{\partial \bar{G}_2}{\partial \hat{n}_2}\right)_{T, p} \hat{n}_1 \hat{n}_2 .$$

Since $\hat{n}_1$ approaches 1 as a limit when $\hat{n}_2$ approaches zero, T, p, and n_1 being held constant, it follows that $\hat{n}_1 \hat{n}_2 \left(\frac{\partial \bar{G}_2}{\partial \hat{n}_2}\right)_{T, p}$ approaches the same limit as $\hat{n}_2\left(\frac{\partial \bar{G}_2}{\partial \hat{n}_2}\right)_{T, p}$ and $n_2\left(\frac{\partial \bar{G}_2}{\partial n_2}\right)_{T, p, n_1}$.

from the equation

$$\left(\frac{\partial G}{\partial m_1}\right)_{T,\,p,\,m_2} = \frac{\vec{G}_1}{A_1} \,, \qquad \text{(III-34)}$$

where A_1 denotes the number of grams in a gram atom of mercury. The intensive function $\breve{G}$ is defined by the equation

$$\breve{G} \equiv \frac{G}{m_1 + m_2} \,. \qquad \text{(III-35)}$$

The derivative $\left(\frac{\partial \breve{G}}{\partial \breve{m}_1}\right)_{T,\,p}$ for liquid thallium amalgams at 20°C and 1 atmosphere can be calculated from the equation

$$\left(\frac{\partial \breve{G}}{\partial \breve{m}_1}\right)_{T,\,p} = \left(\frac{\partial G}{\partial m_1}\right)_{T,\,p,\,m_2} - \left(\frac{\partial G}{\partial m_2}\right)_{T,\,p,\,m_1} . \qquad \text{(III-36)}$$

[11]

By application of the Gibbs-Helmholtz equation

$$1_2 - \hat{H}_2 = NFT \,||\, - NF£ \wedge \qquad \text{(111-37)}$$

where H denotes the enthalpy, $U + pV$, of a liquid thallium amalgam, H_2 denotes the partial derivative $\left(\frac{\partial H}{\partial n_2}\right)_{T,\,p,\,n_1}$ and

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[11] The derivation of equation (XII-36) is given in Appendix A to Part III.

[12] Lewis, G.N., and M. Randall, op. cit., pp. 172-173.

$\hat{H}_2$ the value of the function H for pure crystalline thallium per gram atom, the partial derivative $\bar{H}_2$ for liquid thallium amalgams could then be determined, provided the electromotive forces of the cells be measured over a range of temperature, the value of $\hat{H}_2$ being assumed known from measurements on pure crystalline thallium. From the values of $\bar{H}_2$, the values of $\bar{H}_1 - \hat{H}_1$ are calculable by the use of the equation

$$\bar{H}_1 - \hat{H}_1 = -\int_0^{\hat{n}_2} \frac{\hat{n}_2}{\hat{n}_1} \frac{\partial \bar{H}_2}{\partial \hat{n}_2} d\hat{n}_2 , \qquad \text{(III-38)}$$

where $\bar{H}_1$ denotes the partial derivative $\left(\frac{\partial H}{\partial n_1}\right)_{T, p, n_2}$ and $\hat{H}_1$ the value of the function H for pure mercury per gram atom. The value of $\hat{H}_1$ is assumed to be known from measurements on pure mercury, and hence $\bar{H}_1$ could be obtained as a function of the gram atom fraction at 20°C and 1 atmosphere. The derivative $\left(\frac{\partial H}{\partial m_2}\right)_{T, p, m_1}$ could be calculated from the equation

$$\left(\frac{\partial H}{\partial m_2}\right)_{T, p, m_1} = \frac{\bar{H}_2}{A_2} \qquad \text{(III-39)}$$

and the derivative $\left(\frac{\partial H}{\partial m_1}\right)_{T, p, m_2}$ could be calculated from the equation

$$ \tag{III-40} $$

The intensive function $\breve{H}$ is defined by the equation

$$\breve{H} \equiv \frac{H}{m_1 + m_2} \quad . \tag{III-41}$$

The derivative $\left(\frac{\partial \breve{H}}{\partial \breve{m}_1}\right)_{T,p}$ for liquid thallium amalgams at 20°C and 1 atmosphere could then be calculated from the equation[13]

$$\left(\frac{\partial \breve{H}}{\partial \breve{m}_1}\right)_{T,p} = \left(\frac{\partial H}{\partial m_1}\right)_{T,p,m_2} - \left(\frac{\partial H}{\partial m_2}\right)_{T,p,m_1} \tag{III-42}$$

Alternatively, the function $\breve{H}$ of liquid thallium amalgams and the derivative $\left(\frac{\partial \breve{H}}{\partial \breve{m}_1}\right)_{T,p}$ could be calculated from calorimetric determinations of heats of mixing of thallium and mercury at constant pressure. Finally the values of $\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p}$ and $\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}$ for liquid thallium amalgams at 20°C and 1 atmosphere could be calculated from the equations

$$\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} = \left(\frac{\partial \breve{H}}{\partial \breve{m}_1}\right)_{T,p} - p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} \tag{III-43}$$

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[13] The derivation of equation (III-42) is given in Appendix A to Part III.

and

$$\left(\frac{\partial \breve{S}}{\partial m_1}\right)_{T,\,p} = \frac{1}{T}\left[\left(\frac{\partial \breve{H}}{\partial m_1}\right)_{T,\,p} - \left(\frac{\partial \breve{G}}{\partial m_1}\right)_{T,\,p}\right]. \qquad \text{(III-44)}$$

Derivation of any desired relation between the intensive thermodynamic quantities, T, p, m_1, $\breve{V}$, $\breve{U}$, $\breve{S}$, and their first derivatives for a binary system of one phase from the experimentally determined relations by the use of functional determinants (Jacobians)[14]

Equations (III-5), (III-6), and (III-7) can, in general, be solved for any three of the quantities, T, p, m_1, $\breve{V}$, $\breve{U}$, $\breve{S}$, as functions of the remaining three. The first partial derivative of any one of the quantities, T, p, m_1, $\breve{V}$, $\breve{U}$, $\breve{S}$, with respect to any second quantity when any third and fourth quantities are held constant can be obtained in terms of the six first derivatives, $\frac{\partial \breve{V}}{\partial T}$, $\frac{\partial \breve{V}}{\partial p}$, $\frac{\partial \breve{V}}{\partial m_1}$, $\breve{C}_p$, $\frac{\partial \breve{U}}{\partial m_1}$, $\frac{\partial \breve{S}}{\partial m_1}$, together with the absolute thermodynamic temperature and the pressure, by application of the theorem[15] stating that, if $v = \phi(x, y, z)$, $x = f(u, v, w)$, $y = \psi(u, v, w)$, $z = \chi(u, v, w)$,

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[14] Tunell, G., op. cit., pp. 17-23.

[15] A proof of this theorem for the case of functions of three independent variables is given in Appendix C to Part II.

then one has

$$\left(\frac{\partial x'}{\partial x}\right)_{y,z} = \frac{\begin{vmatrix} \frac{\partial x'}{\partial u} & \frac{\partial x'}{\partial v} & \frac{\partial x'}{\partial w} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \\ \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \end{vmatrix}}{\begin{vmatrix} \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} & \frac{\partial x}{\partial w} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} & \frac{\partial y}{\partial w} \\ \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} & \frac{\partial z}{\partial w} \end{vmatrix}} = \frac{\dfrac{\partial(x', y, z)}{\partial(u, v, w)}}{\dfrac{\partial(x, y, z)}{\partial(u, v, w)}}, \qquad \text{(III-45)}$$

provided all the partial derivatives in the determinants are continuous and provided the determinant in the denominator is not equal to zero.

In Tables III-1 to III-15 the value of the Jacobian is given for each set of three of the variables, T, p, m_1, V, U, S as x', y, z, or x, y, z, and with T, p, m_1 as u, v, w. There are sixty Jacobians in the Table, but one has

$$\frac{\partial(x, y, z)}{\partial(u, v, w)} = -\frac{\partial(z, y, x)}{\partial(u, v, w)} = \frac{\partial(y, z, x)}{\partial(u, v, w)}, \qquad \text{(III-46), (III-47)}$$

because interchanging two rows of a determinant changes the sign of the determinant. Hence it is only necessary to calculate the values of twenty of the sixty Jacobians. The calculations of these twenty Jacobians follow;

$$\frac{\partial(\breve{m}_1, T, p)}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial \breve{m}_1} \end{vmatrix}$$

$$= 1 ; \qquad \text{(III-48)}$$

$$\frac{\partial(\breve{V}, T, p)}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial \breve{m}_1} \end{vmatrix}$$

$$= \left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} ; \qquad \text{(III-49)}$$

$$\frac{\partial(\breve{U}, T, p)}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{U}}{\partial T} & \frac{\partial \breve{U}}{\partial p} & \frac{\partial \breve{U}}{\partial \breve{m}_1} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial \breve{m}_1} \end{vmatrix}$$

$$= \left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} ; \qquad \text{(III-50)}$$

$$\frac{\partial(\breve{S}, T, p)}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} & \frac{\partial \breve{S}}{\partial \breve{m}_1} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial \breve{m}_1} \end{vmatrix}$$

$$= \left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\, p} ; \qquad \text{(III-51)}$$

$$\frac{\partial(\breve{V}, T, \breve{m}_1)}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \end{vmatrix}$$

$$= -\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1} ; \qquad \text{(III-52)}$$

$$\frac{\partial(\breve{U}, T, \breve{m}_1)}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{U}}{\partial T} & \frac{\partial \breve{U}}{\partial p} & \frac{\partial \breve{U}}{\partial \breve{m}_1} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \end{vmatrix}$$

$$= T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1} + p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1} ; \qquad \text{(III-53)}$$

$$\frac{\partial(\breve{S}, T, \breve{m}_1)}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} & \frac{\partial \breve{S}}{\partial \breve{m}_1} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \end{vmatrix}$$

$$= \left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1} ; \qquad \text{(111-54)}$$

$$\frac{\partial(\breve{U}, T, \breve{V})}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{U}}{\partial T} & \frac{\partial \breve{U}}{\partial p} & \frac{\partial \breve{U}}{\partial \breve{m}_1} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \end{vmatrix} \qquad \text{(111-55)}$$

$$= \left[\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\, p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1} + \left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\, p} T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1} ;$$

$$\frac{\partial(\breve{S}, T, \breve{V})}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} & \frac{\partial \breve{S}}{\partial \breve{m}_1} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \end{vmatrix}$$

$$= \left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\, p}\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1} + \left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\, p}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1} ; \qquad \text{(111-56)}$$

$$\frac{\partial(\breve{S}, T, \breve{U})}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} & \frac{\partial \breve{S}}{\partial \breve{m}_1} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial \breve{U}}{\partial T} & \frac{\partial \breve{U}}{\partial p} & \frac{\partial \breve{U}}{\partial \breve{m}_1} \end{vmatrix}$$

$$= \left[\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1} - \left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p} \cdot p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1} ; \qquad \text{(III-57)}$$

$$\frac{\partial(\breve{V}, p, \breve{m}_1)}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial \breve{m}_1} \\ \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \end{vmatrix}$$

$$= \left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1} ; \qquad \text{(III-58)}$$

$$\frac{\partial(\breve{U}, p, \breve{m}_1)}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{U}}{\partial T} & \frac{\partial \breve{U}}{\partial p} & \frac{\partial \breve{U}}{\partial \breve{m}_1} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial \breve{m}_1} \\ \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \end{vmatrix}$$

$$= \breve{C}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1} ; \qquad \text{(III-59)}$$

$$\frac{\partial(\breve{S}, p, \breve{m}_1)}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} & \frac{\partial \breve{S}}{\partial \breve{m}_1} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial \breve{m}_1} \\ \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \end{vmatrix}$$

$$= \frac{\breve{C}_p}{T}, \qquad \text{(III-60)}$$

$$\frac{\partial(\breve{U}, p, \breve{V})}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{U}}{\partial T} & \frac{\partial \breve{U}}{\partial p} & \frac{\partial \breve{U}}{\partial \breve{m}_1} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial \breve{m}_1} \\ \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \end{vmatrix}$$

$$= -\left[\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} + \breve{C}_p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}; \qquad \text{(III-61)}$$

$$\frac{\partial(\breve{S}, p, \breve{V})}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} & \frac{\partial \breve{S}}{\partial \breve{m}_1} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial \breve{m}_1} \\ \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \end{vmatrix}$$

$$= \frac{\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} - \left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}, \qquad \text{(III-62)}$$

$$\frac{\partial(\breve{S}, p, \breve{U})}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} & \frac{\partial \breve{S}}{\partial \breve{m}_1} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial \breve{m}_1} \\ \frac{\partial \breve{U}}{\partial T} & \frac{\partial \breve{U}}{\partial p} & \frac{\partial \breve{U}}{\partial \breve{m}_1} \end{vmatrix}$$

$$= \frac{\breve{C}_p}{T}\left[\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right] + \left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p} p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}; \tag{III-63}$$

$$\frac{\partial(\breve{U}, \breve{m}_1, \breve{V})}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{U}}{\partial T} & \frac{\partial \breve{U}}{\partial p} & \frac{\partial \breve{U}}{\partial \breve{m}_1} \\ \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \\ \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \end{vmatrix}$$

$$= -T\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} - \breve{C}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}; \tag{III-64}$$

$$\frac{\partial(\breve{S}, \breve{m}_1, \breve{V})}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} & \frac{\partial \breve{S}}{\partial \breve{m}_1} \\ \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \\ \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \end{vmatrix}$$

$$= -\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} - \frac{\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}; \tag{III-65}$$

$$\frac{\partial(\breve{S}, \breve{m}_1, \breve{U})}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} & \frac{\partial \breve{S}}{\partial \breve{m}_1} \\ \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \\ \frac{\partial \breve{U}}{\partial T} & \frac{\partial \breve{U}}{\partial p} & \frac{\partial \breve{U}}{\partial \breve{m}_1} \end{vmatrix}$$

$$= p\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\, \breve{m}_1} + \frac{p\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1}; \qquad \text{(III-66)}$$

$$\frac{\partial(\breve{S}, \breve{V}, \breve{U})}{\partial(T, p, \breve{m}_1)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} & \frac{\partial \breve{S}}{\partial \breve{m}_1} \\ \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \\ \frac{\partial \breve{U}}{\partial T} & \frac{\partial \breve{U}}{\partial p} & \frac{\partial \breve{U}}{\partial \breve{m}_1} \end{vmatrix}$$

(III-67)

$$= \left[\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\, p}\right]\left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\, \breve{m}_1} + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1}\right].$$

Table III-l
Jacobians of intensive functions
for a binary system of one phase

d(x', y, z) / 3(7\ p, m O ' 3(x, v, z) / 3(T, p, ŏ O

\y» z X'N. x N	T, p
Si	1
V̌	(ĬS)
ŭ	(ft)
%J S	(ĭs)

Table III-2
Jacobians of intensive functions
for a binary system of one phase

$$\frac{\partial(x', y, z)}{\partial(T, p, \breve{m}_1)} \qquad \frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)}$$

x', x \ y, z	$T, \breve{m}_1$
p	-1
$\breve{V}$	$-\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$
$\breve{V}$	$T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} + p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$
$\breve{S}$	$\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}$

Table III-3
Jacobians of intensive functions
for a binary system of one phase

$$\frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)} \cdot \frac{\partial(T, y, z)}{\partial(T, p, \breve{m}_1)}$$

x \ y, z	$T, \breve{V}$
p	$-\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}$
[illegible]	$\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$
$\breve{U}$	$\left[\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1} + \left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} \cdot T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}$
$\breve{S}$	$\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} + \left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$

Table III-4
Jacobians of intensive functions
for a binary system of one phase

$$\frac{\partial(x', y, z)}{\partial(T, p, \breve m_1)}, \quad \frac{\partial(x, y, z)}{\partial(T, p, \breve m_1)}$$

x', x \ y, z	$T, \breve U$
p	$-\left(\frac{\partial \breve U}{\partial \breve m_1}\right)_{T,p}$
$\breve m_1$	$-T\left(\frac{\partial \breve V}{\partial T}\right)_{p,\breve m_1} - p\left(\frac{\partial \breve V}{\partial p}\right)_{T,\breve m_1}$
$\breve V$	$\left[-\left(\frac{\partial \breve U}{\partial \breve m_1}\right)_{T,p} - p\left(\frac{\partial \breve V}{\partial \breve m_1}\right)_{T,p}\right]\left(\frac{\partial \breve V}{\partial p}\right)_{T,\breve m_1} - \left(\frac{\partial \breve V}{\partial \breve m_1}\right)_{T,p} T\left(\frac{\partial \breve V}{\partial T}\right)_{p,\breve m_1}$
$\breve S$	$\left[\left(\frac{\partial \breve U}{\partial \breve m_1}\right)_{T,p} - T\left(\frac{\partial \breve S}{\partial \breve m_1}\right)_{T,p}\right]\left(\frac{\partial \breve V}{\partial T}\right)_{p,\breve m_1} - \left(\frac{\partial \breve S}{\partial \breve m_1}\right)_{T,p} \cdot p\left(\frac{\partial \breve V}{\partial p}\right)_{T,\breve m_1}$

Table III-5
Jacobians of intensive functions
for a binary system of one phase

$$\frac{\partial(x', y, z)}{\partial(T, p, \breve{m}_1)} = \frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)}$$

$x \backslash y, z$	$T, \breve{S}$
p	$-\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}$
$\breve{m}_1$	$-\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}$
[illegible]	$-\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1} - \left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}$
$\breve{U}$	$\left[-\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1} + \left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p} \cdot p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}$

Table III-6
Jacobians of intensive functions
for a binary system of one phase

3(x', y, z) / d(T, p, m̆i) f 3(x, y, z) / 3(T,pfrăi)

x'\ x	p,fIfx
T	1
V̆	(dV̆)
ŭ	c̆p-P\3̄r̄j - p. mi
s̆	f̆a r

Table III-7
Jacobians of intensive functions
for a binary system of one phase

$$\frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)}$$

y, z / x	p, p
T	$\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}$
$\breve{m}_1$	[illegible] p. mi
U	[- U*J_T, p" pfeJ_T, J l a? I_Si + cpfej_r, p
$\breve{S}$	rl»J_T,p UxJ_r,p U;_p>Ji

Table III-8
Jacobians of intensive functions
for a binary system of one phase

3(x', vt z) f 3(x, v, z)
3(T, p, tfi) 3(T, p.tfi)

\vf, z / x	p, (̆/
T	$\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p}$
$\breve{m}_1$	-cP̆ + K3?j -
V	[/BŎX (%̆V \ l/a?\ w/3?\ [U) n p * His,),.. Jvw),, ft - 'pfej r, p
S	l[(f̆,) 7.p -Ki,),J*(f̆,) r.;Kii,,

Table III-9
Jacobians of intensive functions
for a binary system of one phase

$$\frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)}, \quad \frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)}$$

x \ y, z	$p, \breve{S}$
T	$\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}$
[illegible]	$\frac{\breve{c}_p}{T}$
$\breve{V}$	$-\frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} + \left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}$
$\breve{U}$	$-\frac{\breve{c}_p}{T}\left[\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right] - \left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p} \cdot p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}$

Table 111-10
Jacobians of intensive functions
for a binary system of one phase

$\underline{d(x', y, z)}$ $\underline{d(x, y, z)}$
3(7, p.Afi) J 3(7, p, »i)

x	$\breve{m}_1, \breve{V}$
T	$-\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1}$
P	$\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1}$
U	JdV̆)^2 - ^\
$\breve{S}$	$-\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\, \breve{m}_1} - \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1}$

Table III-11
Jacobians of intensive functions
for a binary system of one phase

$$\frac{\partial(x', y, z)}{\partial(T, p, \breve{m}_1)} ; \frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)}$$

y, z \ x	mi, ff
T	$T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} + p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$
P	'p, mi
$\breve{V}$	$T\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} + \breve{c}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$
$\breve{S}$	$p\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} + \frac{p\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$

Table III-12
Jacobians of intensive functions
for a binary system of one phase

$$\frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)}, \quad \frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)}$$

y, z / x	$\breve{m}_1, \breve{S}$
T	$\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}$
P	$\breve{r}$
V	$\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} + \frac{\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$
S	[illegible]

Table III-13
Jacobians of intensive functions
for a binary system of one phase

$$\frac{\partial(x,\, y,\, z)}{\partial(T,\, p,\, \breve{m}_1)} \qquad \frac{\partial(x,\, y,\, z)}{\partial(T,\, p,\, \breve{m}_1)}$$

x \ y, z	$\breve{V}, \breve{U}$
T	$\left[\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1} + \left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T}$ [illegible]
p	$\left[-\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} - p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1} + \breve{c}_p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}$
$\breve{m}_1$	$-T\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\,\breve{m}_1} - \breve{c}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}$
$\breve{S}$	$\left[\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p}\right]\left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\,\breve{m}_1} + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right]$

Table III-14
Jacobians of intensive functions
for a binary system of one phase

$$\frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)} \;,\; \frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)}$$

$x \backslash y, z$	$\breve{V}, \breve{S}$
T	$\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1} + \left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}$
p	$\frac{\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - \left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}$
$\breve{m}_1$	$-\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} - \frac{\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}$
[illegible]	$\left[-\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} - p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} + T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]\left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} + \frac{\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right]$

Table III-15
Jacobians of intensive functions
for a binary system of one phase

$$\frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)} \quad , \quad \frac{\partial(x, y, z)}{\partial(T, p, \breve{m}_1)}$$

y, z / x	$\breve{U}, \breve{S}$
T	[illegible] $\left(\frac{\partial \breve{K}}{\partial p}\right)$ [illegible]
p	$\frac{\breve{c}_p}{T}\left[\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p}$ [illegible] $T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]$ [illegible] $\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}$ [illegible] $p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}$
$\breve{m}_1$	$p\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} + \frac{p\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}$
$\breve{y}$	[illegible] $+ \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,}$ [illegible]

In order to obtain the first partial derivative of any one of the six quantities, $T, p, \breve{m}_i, \breve{V}, \breve{U}, \breve{S}$, with respect to any second quantity of the six when any third and fourth quantities of the six are held constant, one has only to divide the value of the Jacobian in which the first letter in the first line is the quantity being differentiated and in which the second and third letters in the first line are the quantities held constant by the value of the Jacobian in which the first letter of the first line is the quantity with respect to which the differentiation is taking place and in which the second and third letters in the first line are the quantities held constant.

To obtain the relation among any seven derivatives, having expressed them in terms of the same six derivatives,

$$\left(\frac{\partial \breve{V}}{\partial T}\right) \quad \left(\partial \breve{V}\right) \quad \left(\partial \breve{V}\right) \quad - \quad \left(\breve{W}\right)_p \quad \left(\partial \breve{S}\right)_{T,p} ,$$

one can then eliminate the six derivatives from the seven equations, leaving a single equation connecting the seven derivatives. In addition to the relations among seven derivatives there are also degenerate cases in which there are relations among fewer than seven derivatives.

An additional therraodynamic function $A \equiv U - TS$ is used to facilitate the solution of many problems. The corresponding intensive function $\breve{A}$ is defined by the equation

$$1\ s\ \mathrm{S7}\overset{A}{\mathrm{T}}1£ \ \bullet \qquad (\mathrm{m\_68})$$

In case a relation is needed that involves one or more of the thermodynamic potential functions, *H, A*, or *G*, partial derivatives involving one or more of these functions can also be calculated as the quotients of two Jacobians, which can themselves be evaluated by the same method used to calculate the Jacobians in Tables III-l to 111-15.

Proof of the relation

$$\left(\frac{\partial \breve{G}}{\partial \breve{m}_1}\right)_{T,p} \qquad\qquad {}_{T,p,m_2} - \left(\frac{\partial G}{\partial m_2}\right)_{T,p,m_1}$$ [1]

The quantity $\breve{G}$ is defined by the equation

$$\breve{G} \equiv \frac{G}{\quad} \quad . \qquad \text{(III-A-1)}$$

Multiplying both sides of equation (III-A-1) by (/??! + m_2) one has

$$G = \breve{G}(m_1 + m_2) \quad . \qquad \text{(III-A-2)}$$

Differentiating both sides of equation (III-A-2) with respect to *ai* holding T, p, and roa fast one obtains

$$\left(\quad {}_{T,p,m_2} \qquad\qquad \right)_{T,p,m_2} \quad . \qquad \text{(III-A-3)}$$

The quantity *&* is a function of the temperature T» the pressure p* and the mass fraction $\breve{m}_1$. By application of the theorem for change of variables in partial differentiation one has thus

$$\left(\frac{\partial \breve{G}}{\partial m}\right)_{T,p,m_2} = \left(\frac{\partial \breve{G}}{\partial \breve{m}_1}\right)_{T,p}\left(\frac{\partial \breve{m}_1}{\partial m_1}\right)_{T,p,m_2} \quad , \qquad \text{(III-A-4)}$$

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[1] Tunell, G., Amer, Jour. Sci., 255, 261-265, 1957, and Tunell, G,, *Relations between Intensive Thermodynamic Quantities and Their First Derivatives in a Binary System of One Phaset* W.H. Freeman and Co., San Francisco and London, 1960, pp. 25, 26.

Since, by definition,

$$\breve{m}_1 \equiv \frac{m_1}{m_1 + m_2} \quad , \qquad \text{(III-A-5)}$$

one has

$$\left(\frac{\partial \breve{m}_1}{\partial m_1}\right)_{T,\,p,\,m_2} = \frac{1}{m_1 + m_2} - \frac{m_1}{(m_1 + m_2)^2}$$

$$= \frac{m_2}{(m_1 + m_2)^2} \quad . \qquad \text{(III-A-6)}$$

Hence it follows that

$$\left(\frac{\partial G}{\partial m_1}\right)_{T,\,p,\,m_2} = \breve{G} + (m_1 + m_2)\left(\frac{\partial \breve{G}}{\partial \breve{m}_1}\right)_{T,\,p} \frac{m_2}{(m_1 + m_2)^2}$$

$$= \breve{G} + \breve{m}_2\left(\frac{\partial \breve{G}}{\partial \breve{m}_1}\right)_{T,\,p} \quad , \qquad \text{(III-A-7)}$$

and, similarly,

$$\left(\frac{\partial G}{\partial m_2}\right)_{T,\,p,\,m_1} = \breve{G} + \breve{m}_1\left(\frac{\partial \breve{G}}{\partial \breve{m}_2}\right)_{T,\,p}$$

$$= \breve{G} - \breve{m}_1\left(\frac{\partial \breve{G}}{\partial \breve{m}_1}\right)_{T,\,p} \quad . \qquad \text{(III-A-8)}$$

By subtracting the left side of equation (III-A-8) from the left side of equation (III-A-7) and the right side of equation (III-A-8) from the right side of equation (III-A-7), one thus obtains the equation to be proved:

$$\left(\frac{\partial \breve{G}}{\partial \breve{m}_1}\right)_{T,\,p} = \left(\frac{\partial G}{\partial m_1}\right)_{T,\,p,\,m_2} - \left(\frac{\partial G}{\partial m_2}\right)_{T,\,p,\,m_1} . \qquad \text{(III-A-9)}$$

In a similar way the equation

$$\left(\frac{\partial \breve{H}}{\partial \breve{m}_1}\right)_{T,\,p} = \left(\frac{\partial H}{\partial m_1}\right)_{T,\,p,\,m_2} - \left(\frac{\partial H}{\partial m_2}\right)_{T,\,p,\,m_1} \qquad \text{(III-A-10)}$$

can also be derived.

Appendix B to Part III

Transformation of the work and heat line integrals from one coordinate space to other coordinate spaces in the case of a binary system of one phase and of unit mass

As in the case of a one component system of one phase and of variable mass, it is also true in the case of a binary system of one phase and of unit mass that it is not necessary to define either work or heat when masses are being transferred to or from the system to change its composition in order to obtain the energy and the entropy as functions of the absolute thermodynamic temperature, the pressure, and the mass fraction of one component from experimental measurements. Thus the derivation of the Jacobians listed in Tables III-l to III—15 did not depend upon definitions of work or heat in the case of a binary system of one phase and of unit mass when masses are being transferred to or from the system to change its composition.

For some purposes, however, it is useful to have definitions of work done and heat received in the case of a binary system of one phase and of unit mass when masses are being transferred to or from the system to change its composition. If the conclusion of Van Wylen and Professor Uild be accepted that it cannot be said that work is done at a stationary boundary across which mass is transported, then the work *I'!* done by a binary system of one phase and of unit mass can be represented by the line integral

$$\int_{T_0,\, p_0,\, \breve{m}_{1_0}}^{T,\, p,\, \breve{m}_1} \left\{ p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1} dT + p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1} dp + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\, p} d\breve{m}_1 \right\} \quad \text{(III-B-1)}$$

in $(T, p, \breve{m}_1)$-space. Furthermore, in the case of such a system the heat Q received can be represented by the line integral

$$Q = \int_{T_0,\, p_0,\, \breve{m}_{1_0}}^{T,\, p,\, \breve{m}_1} \left\{ \left(\frac{dQ}{dT}\right)_{p,\, \breve{m}_1} dT + \left(\frac{dQ}{dp}\right)_{T,\, \breve{m}_1} dp + \left(\frac{dQ}{d\breve{m}_1}\right)_{T,\, p} d\breve{m}_1 \right\}$$

$$\int_{\ldots\, \breve{m}_{1_0}}^{T,\, p,\, \breve{m}_1} \Big\{ \cdots \Big)_{T,\, p} d\breve{m}_1 \Big\} . \quad \text{(III-B-2)}$$

In order to obtain the total derivative of the work done along a straight line parallel to one of the coordinate axes in any other coordinate space one obtains from Tables III-1 to III-15 the partial derivative of the volume with respect to the quantity plotted along, that axis when the quantities plotted along the other axes are held constant and one multiplies this partial derivative by the pressure. The total derivative of the heat received along a straight line parallel to one of the coordinate axes in any other space, on the other hand, cannot be obtained by multiplication of the partial derivative of the entropy by the absolute thermodynamic temperature when transfer of masses to or from the system is involved. In such cases the total derivatives of the heat received along lines parallel to the coordinate axes in any desired coordinate space can be derived in terms of the total derivatives of the heat received along lines parallel to the coordinate axes in $(T, p, \breve{m}_1)$-space by transformation of the heat line integrals by the use of the method set forth in the second half of Appendix B to Part II. Following is an example of such a transformation. In the case of a binary system of one phase and of unit mass the heat line integral extended along a path in $(T, \breve{m}_1, \breve{V})$-space is

$$Q = \int_{T_0,\, \breve{m}_{1_0},\, \breve{V}_0}^{T,\, \breve{m}_1,\, \breve{V}} \left\{ \left(\frac{dQ}{dT}\right)_{\breve{m}_1,\, \breve{V}} dT + \left(\frac{dQ}{d\breve{m}_1}\right)_{T,\, \breve{V}} d\breve{m}_1 + \left(\frac{dQ}{d\breve{V}}\right)_{T,\, \breve{m}_1} d\breve{V} \right\}$$

$$= \int_{T_0,\, \breve{m}_{1_0},\, \breve{V}_0}^{T,\, \breve{m}_1,\, \breve{V}} \left\{ \breve{c}_V dT + \left(\frac{dQ}{d\breve{m}_1}\right)_{T,\, \breve{V}} d\breve{m}_1 + l_V d\breve{V} \right\} . \qquad \text{(III-B-3)}$$

The derivatives $\left(\frac{\partial Q}{\partial T}\right)_{\breve{m}_1,\, \breve{V}}$, $\left(\frac{\partial Q}{\partial \breve{m}_1}\right)_{T,\, \breve{V}}$, and $\left(\frac{\partial Q}{\partial \breve{V}}\right)_{T,\, \breve{m}_1}$ can be evaluated by the method set forth in the second half of Appendix B to part II as the quotients of two determinants. Thus we have

$$\left(\frac{\partial Q}{\partial T}\right)_{\breve{m}_1,\, \breve{V}} = \breve{c}_v = \frac{\begin{vmatrix} \frac{\partial Q}{\partial T} & \frac{\partial Q}{\partial p} & \frac{\partial Q}{\partial \breve{m}_1} \\ \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \\ \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \end{vmatrix}}{\begin{vmatrix} \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \\ \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \end{vmatrix}}$$

$$= \left[\left(\frac{\partial Q}{\partial p}\right)_{T,\, \breve{m}_1}\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1} - \left(\frac{\partial Q}{\partial T}\right)_{p,\, \breve{m}_1}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1}\right] \div \left[-\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1}\right]$$

$$= \left[\breve{c}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1} - \breve{l}_p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1}\right] \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1}$$

$$= \left[\breve{c}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1} + T\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\, \breve{m}_1}\right] \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1}, \qquad \text{(III-B-4)}$$

and

$$\left(\frac{\partial Q}{\partial \breve{m}_1}\right)_{T,\,\breve{V}} = \frac{\begin{vmatrix} \dfrac{\partial Q}{\partial T} & \dfrac{\partial Q}{\partial p} & \dfrac{\partial Q}{\partial \breve{m}_1} \\[2ex] \dfrac{\partial T}{\partial T} & \dfrac{\partial T}{\partial p} & \dfrac{\partial T}{\partial \breve{m}_1} \\[2ex] \dfrac{\partial \breve{V}}{\partial T} & \dfrac{\partial \breve{V}}{\partial p} & \dfrac{\partial \breve{V}}{\partial \breve{m}_1} \end{vmatrix}}{\begin{vmatrix} \dfrac{\partial \breve{m}_1}{\partial T} & \dfrac{\partial \breve{m}_1}{\partial p} & \dfrac{\partial \breve{m}_1}{\partial \breve{m}_1} \\[2ex] \dfrac{\partial T}{\partial T} & \dfrac{\partial T}{\partial p} & \dfrac{\partial T}{\partial \breve{m}_1} \\[2ex] \dfrac{\partial \breve{V}}{\partial T} & \dfrac{\partial \breve{V}}{\partial p} & \dfrac{\partial \breve{V}}{\partial \breve{m}_1} \end{vmatrix}}$$

$$= \left[\left(\frac{\partial Q}{\partial \breve{m}_1}\right)_{T,\,p}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1} - \left(\frac{\partial Q}{\partial p}\right)_{T,\,\breve{m}_1}\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}\right] \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}$$

$$= \left[\left(\frac{\partial Q}{\partial \breve{m}_1}\right)_{T,\,p}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1} - \ell_p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}\right] \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}$$

$$= \left[\left(\frac{\partial Q}{\partial \breve{m}_1}\right)_{T,\,p}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1} + T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}\right] \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}$$

(III-B-5)

and finally

$$\left(\frac{\partial \breve{Q}}{\partial \breve{V}}\right)_{T,\,\breve{m}_1} = \breve{l}_V = \frac{\begin{vmatrix} \frac{\partial \breve{Q}}{\partial T} & \frac{\partial \breve{Q}}{\partial p} & \frac{\partial \breve{Q}}{\partial \breve{m}_1} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \end{vmatrix}}{\begin{vmatrix} \frac{\partial \breve{V}}{\partial T} & \frac{\partial \breve{V}}{\partial p} & \frac{\partial \breve{V}}{\partial \breve{m}_1} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} \\ \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} \end{vmatrix}}$$

$$= \left[-\left(\frac{\partial \breve{Q}}{\partial p}\right)_{T,\,\breve{m}_1}(1)\right] \div \left[-\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right]$$

$$= \left[\breve{l}_p\right] \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}$$

$$= \left[-T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}\right] \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1} . \qquad \text{(III-B-6)}$$

Part IV

Relations between thermodynamic quantities and their first derivatives in a binary system of one phase and of variable total mass

Introduction

In the following text the relations for the energy and the entropy of a binary system of one phase and of variable total mass are derived and a table of Jacobians is presented by means of which any first partial derivative of any one of the quantities, absolute thermodynamic temperature T, pressure p, mass m_1 of component 1, mass m_2 of component 2, total volume V, total energy U, and total entropy S, with respect to any other of these quantities can be obtained in terms of the partial derivative of the specific volume V with respect to the absolute thermodynamic temperature, the partial derivative of the specific volume with respect to the pressure, the partial derivative of the specific volume with respect to the mass fraction $\breve{m}_1$ of component 1, the heat capacity at constant pressure per unit of mass $\breve{C}_p$, the partial derivative of the specific energy $\breve{U}$ with respect to the mass fraction of component 1, the partial derivative of the specific entropy $\breve{S}$ with respect to the mass fraction of component 1, and certain of the quantities, T, p, m_1, m_2, $\breve{m}_1$, $\breve{m}_2$, $\breve{V}$, $\breve{U}$, $\breve{S}$, where $\breve{m}_2$ denotes the mass fraction of component 2.

Calculation of the total volume, the total energy, and the total entropy of a binary system of one phase and of variable total mass as functions of the absolute thermodynamic temperature, the pressure, and the masses of components *one* and two

Thermodynamic formulas can be developed in the case of a binary system of one phase and of variable total mass on the basis of the following set of variable quantities: the absolute thermodynamic temperature, the pressure, the mass of component 1, the mass of component 2, the total volume, the total energy, the total entropy, the mass fraction of component 1, the mass fraction of component 2, the specific volume, the specific energy, the specific entropy, the heat capacity at constant pressure per unit of mass, and the latent heat of change of pressure at constant temperature per unit of mass (p.

In the case of a binary system of one phase and of variable total mass the total volume is a function of the absolute thermodynamic temperature, the pressure, the mass of component 1, and the mass of component 2,

$$V = f(T, p, m_1, m_2) . \qquad \text{(IV-1)}$$

The total volume is equal to the total mass times the specific volume

$$V = (m_1 + m_2)\breve{V} , \qquad \text{(IV-2)}$$

and the specific volume is a function of the absolute thermodynamic temperature, the pressure, and the mass fraction of component 1,

$$\breve{V} = \breve{V}(T, p, \breve{m}_1) \ . \tag{IV-3}$$

From equations (IV-1), (IV-2), and (IV-3) it then follows that

$$\left(\frac{\partial V}{\partial T}\right)_{p, m_1, m_2} = (m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} , \tag{IV-4}$$

$$\left(\frac{\partial V}{\partial p}\right)_{T, m_1, m_2} = (m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1} , \tag{IV-5}$$

$$\left(\frac{\partial V}{\partial m_1}\right)_{T, p, m_2} = \breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} , \tag{IV-6}$$

and

$$\left(\frac{\partial V}{\partial m_2}\right)_{T, p, m_1} = \breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} . \tag{IV-7}$$

The total energy is a function of the absolute thermodynamic temperature, the pressure, the mass of component 1, and the mass of component 2

$$U = U(T, p, m_1, m_2) \ . \tag{IV-8}$$

As in the case of a one–component system of one phase and of variable mass it is known from experiment that the energy is an extensive function* Thus the total energy is equal to the total mass times the specific energy

$$U = (m_1 + m_2)\breve{U} \;. \tag{IV-9}$$

Furthermore it is known that the specific energy is a function of the absolute thermodynaraic temperature, the pressure, and the mass fraction of component 1,

$$\breve{U} = \theta(T, p, \breve{m}_1) \;. \tag{IV-10}$$

Thus the relation of the total energy to the absolute thermodynamic temperature, the pressure, the mass of component 1, and the mass of component 2 is expressed by the equation

$$U(T, p, m_1, m_2) - U(T_0, p_0, m_{1_0}, m_{2_0})$$

$$= \int_{T_0, p_0, m_{1_0}, m_{2_0}}^{T, p, m_1, m_2} \left\{ (m_1 + m_2)\left[c_p - p\frac{\partial \breve{v}}{\partial T}\right] dT + (m_1 + m_2)\left[\breve{l}_p - p\frac{\partial \breve{v}}{\partial p}\right] dp \right.$$

$$\left. + \frac{\partial U}{\partial m_1} dm_1 + \frac{\partial U}{\partial m_2} dm_2 \right\} . \tag{IV-11}$$

From equations (IV-8), (IV-9), (IV-10), and (IV-11) it

follows that

$$\left(\frac{\partial U}{\partial T}\right)_{p,\, m_1,\, m_2} = (m_1 + m_2)\left[\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1}\right], \qquad \text{(IV-12)}$$

$$\left(\frac{\partial U}{\partial p}\right)_{T,\, m_1,\, m_2} = (m_1 + m_2)\left[\breve{l}_p - p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1}\right], \qquad \text{(IV-13)}$$

$$\left(\frac{\partial U}{\partial m_1}\right)_{T,\, p,\, m_2} = \breve{U} + \breve{m}_2\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\, p}, \qquad \text{(IV-14)}$$

and

$$\left(\frac{\partial U}{\partial m_2}\right)_{T,\, p,\, m_1} = \breve{U} - \breve{m}_1\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\, p}. \qquad \text{(IV-15)}$$

The total entropy is a function of the absolute thermodynamic temperature, the pressure, the mass of component 1, and the mass of component 2

$$S = S(T,\ p,\ m_1,\ m_2)\,. \qquad \text{(IV-16)}$$

As in the case of a one-component system of one phase and of variable mass it is known from experiment that the entropy is an extensive function. Thus the total entropy is equal to the total mass times the specific entropy

$$S = (m_1 + m_2)\breve{S} \; . \qquad \text{(IV-17)}$$

Furthermore it is known that the specific entropy is a function of the absolute thermodynamic temperature, the pressure, and the mass fraction of component 1,

$$\breve{S} = \phi(T, p, \breve{m}_1) \; . \qquad \text{(IV-18)}$$

Thus the relation of the total entropy to the absolute thermodynamic temperature, the pressure, the mass of component 1, and the mass of component 2 is expressed by the equation

$$S(T, p, m_1, m_2) - S(T_0, p_0, m_{1_0}, m_{2_0})$$

$$= \int_{T_0, p_0, m_{1_0}, m_{2_0}}^{T, p, m_1, m_2} \left\{ (m_1 + m_2)\frac{\breve{C}_p}{T} dT + (m_1 + m_2)\frac{\breve{l}_p}{T} dp \right.$$

$$\left. + \frac{\partial S}{\partial m_1} dm_1 + \frac{\partial S}{\partial m_2} dm_2 \right\} . \qquad \text{(IV-19)}$$

From equations (IV-16), (IV-17), (IV-18), and (IV-19) it follows that

$$\left(\frac{\partial S}{\partial T}\right)_{p,\, m_1,\, m_2} = (m_1 + m_2)\frac{\breve{c}_p}{T}\,, \tag{IV-20}$$

$$\left(\frac{\partial S}{\partial p}\right)_{T,\, m_1,\, m_2} = (m_1 + m_2)\frac{\breve{l}_p}{T}\,, \tag{IV-21}$$

$$\left(\frac{\partial S}{\partial m_1}\right)_{T,\, p,\, m_2} = \breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\, p}\,, \tag{IV-22}$$

and

$$\left(\frac{\partial S}{\partial m_2}\right)_{T,\, p,\, m_1} = \breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\, p}\,. \tag{IV-23}$$

Necessary and sufficient conditions for (IV-11) are

$$\left\{\frac{\partial\left[(m_1 + m_2)\left(\breve{l}_p - p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1}\right)\right]}{\partial T}\right\}_{p,\, m_1,\, m_2}$$

$$= \left\{\frac{\partial\left[(m_1 + m_2)\left(\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1}\right)\right]}{\partial p}\right\}_{T,\, m_1,\, m_2}\,, \tag{IV-24}$$

$$\left\{\frac{\partial\left(\frac{\partial U}{\partial m_1}\right)_{T, p, m_2}}{\partial T}\right\}_{p, m_1, m_2}$$

$$= \left\{\frac{\partial\left[(m_1 + m_2)\left(\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\right)\right]}{\partial m_1}\right\}_{T, p, m_2}, \qquad \text{(IV-25)}$$

$$\left\{\frac{\partial\left(\frac{\partial U}{\partial m_2}\right)_{T, p, m_1}}{\partial T}\right\}_{p, m_1, m_2}$$

$$= \left\{\frac{\partial\left[(m_1 + m_2)\left(\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\right)\right]}{\partial m_2}\right\}, \qquad \text{(IV-26)}$$

$$\left\{\frac{\partial\left(\frac{\partial U}{\partial m_1}\right)_{T, p, m_2}}{\partial p}\right\}_{T, m_1, m_2}$$

$$= \left\{\frac{\partial\left[(m_1 + m_2)\left(\breve{l}_p - p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right)\right]}{\partial m_1}\right\}_{T, p, m_2}, \qquad \text{(IV-27)}$$

$$\left\{\frac{\partial\left(\frac{\partial U}{\partial m_2}\right)_{T,\,p,\,m_1}}{\partial p}\right\}_{T,\,m_1,\,m_2}$$

$$= \left\{\frac{\partial\left[(m_1 + m_2)\left(\breve{l}_p - p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,m_1,\,m_2}\right)\right]}{\partial m_2}\right\}_{T,\,p,\,m_1}, \qquad \text{(IV-28)}$$

and

$$\left\{\frac{\partial\left(\frac{\partial U}{\partial m_1}\right)_{T,\,p,\,m_2}}{\partial m_2}\right\}_{T,\,p,\,m_1} = \left\{\frac{\partial\left(\frac{\partial U}{\partial m_2}\right)_{T,\,p,\,m_1}}{\partial m_1}\right\}_{T,\,p,\,m_2}. \qquad \text{(IV-29)}$$

Similarly, necessary and sufficient conditions for (IV-19) are

$$\left\{\frac{\partial\left[(m_1 + m_2)\frac{\breve{l}_p}{T}\right]}{\partial T}\right\}_{p,\,m_1,\,m_2} = \left\{\frac{\partial\left[(m_1 + m_2)\frac{\breve{c}_p}{T}\right]}{\partial p}\right\}_{T,\,m_1,\,m_2}, \qquad \text{(IV-30)}$$

$$\left\{\frac{\partial\left(\frac{\partial S}{\partial m_1}\right)_{T,\,p,\,m_2}}{\partial T}\right\} = \left\{\frac{\partial\left[(m_1 + m_2)\frac{\breve{c}_p}{T}\right]}{\partial m_1}\right\}_{T,\,p,\,m_2}, \qquad \text{(IV-31)}$$

$$\left\{\frac{\partial\left(\frac{\partial S}{\partial m_2}\right)_{T,\,p,\,m_1}}{\partial T}\right\}_{p,\,m_1,\,m_2} = \left\{\frac{\partial\left[(m_1 + m_2)\frac{\breve{c}_p}{T}\right]}{\partial m_2}\right\}_{T,\,p,\,m_1}, \quad \text{(IV-32)}$$

$$\left\{\frac{\partial\left(\frac{\partial S}{\partial m_1}\right)_{T,\,p,\,m_2}}{\partial p}\right\}_{T,\,m_1,\,m_2} = \left\{\frac{\partial\left[(m_1 + m_2)\frac{\breve{l}_p}{T}\right]}{\partial m_1}\right\}_{T,\,p,\,m_2}, \quad \text{(IV-33)}$$

$$\left\{\frac{\partial\left(\frac{\partial S}{\partial m_2}\right)_{T,\,p,\,m_1}}{\partial p}\right\}_{T,\,m_1,\,m_2} = \left\{\frac{\partial\left[(m_1 + m_2)\frac{\breve{l}_p}{T}\right]}{\partial m_2}\right\}_{T,\,p,\,m_1}, \quad \text{(IV-34)}$$

and

$$\left\{\frac{\partial\left(\frac{\partial S}{\partial m_1}\right)_{T,\,p,\,m_2}}{\partial m_2}\right\}_{T,\,p,\,m_1} = \left\{\frac{\partial\left(\frac{\partial S}{\partial m_2}\right)_{T,\,p,\,m_1}}{\partial m_1}\right\}_{T,\,p,\,m_2}. \quad \text{(IV-35)}$$

Carrying out the indicated differentiations in equation (IV-24) one has

$$(m_1 + m_2)\left[\left(\frac{\partial \breve{l}_p}{\partial T}\right)_{p,\,m_1,\,m_2} - p\left(\frac{\partial\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}}{\partial T}\right)_{p,\,m_1,\,m_2}\right]$$

$$= (m_1 + m_2)\left[\left(\frac{\partial \breve{c}_p}{\partial p}\right)_{T,\,m_1,\,m_2} - p\left(\frac{\partial\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}}{\partial p}\right)_{T,\,m_1,\,m_2} - \left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}\right].$$

(IV-36)

Making use of the change of variable theorem in partial differentiation one obtains

$$\left(\frac{\partial \breve{l}_p}{\partial T}\right)_{p, m_1, m_2} = \left(\frac{\partial \breve{l}_p}{\partial T}\right)_{p, \breve{m}_1} \left(\frac{\partial T}{\partial T}\right)_{p, m_1, m_2} + \left(\frac{\partial \breve{l}_p}{\partial p}\right)_{T, \breve{m}_1} \left(\frac{\partial p}{\partial T}\right)_{p, m_1, m_2} + \left(\frac{\partial \breve{l}_p}{\partial \breve{m}_1}\right)_{T, p} \left(\frac{\partial \breve{m}_1}{\partial T}\right)_{p, m_1, m_2} . \tag{IV-37}$$

The derivatives $\left(\frac{\partial p}{\partial T}\right)_{p, m_1, m_2}$ and $\left(\frac{\partial \breve{m}_1}{\partial T}\right)_{p, m_1, m_2}$ are each equal to zero. Thus one has

$$\left(\frac{\partial \breve{l}_p}{\partial T}\right)_{p, m_1, m_2} = \left(\frac{\partial \breve{l}_p}{\partial T}\right)_{p, \breve{m}_1} . \tag{IV-38}$$

Similarly it follows that

$$\left(\frac{\partial \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}}{\partial T}\right)_{p, m_1, m_2} = \left(\frac{\partial \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}}{\partial T}\right)_{p, \breve{m}_1} = \frac{\partial^2 \breve{V}}{\partial T \partial p} , \tag{IV-39}$$

also

$$\left(\frac{\partial \breve{c}_p}{\partial p}\right)_{T, m_1, m_2} = \left(\frac{\partial \breve{c}_p}{\partial p}\right)_{T, \breve{m}_1} \tag{IV-40}$$

and

$$\left(\frac{\partial\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}}{\partial p}\right)_{T,m_1,m_2} = \left(\frac{\partial\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}}{\partial p}\right)_{T,\breve{m}_1} = \frac{\partial^2 \breve{V}}{\partial p\,\partial T}\;. \tag{IV-41}$$

Consequently substituting the values of $\left(\frac{\partial l_2}{\partial T}\right)_{p,m_1,m_2}$,

$\left(\frac{\partial\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}}{\partial T}\right)$, $\left(\frac{\partial \breve{c}_p}{\partial p}\right)_{T,m_1,m_2}$, and $\left(\frac{\partial\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}}{\partial p}\right)_{T,\breve{m}_1}$

from equations (IV-38), (IV-39), (IV-40), and (IV-41) in equation (IV-36) one obtains

$$\frac{\partial \breve{l}_2}{\partial T} - p\frac{\partial^2 \breve{V}}{\partial T\,\partial p} = \frac{\partial \breve{c}_p}{\partial p} - p\frac{\partial^2 \breve{V}}{\partial p\,\partial T} - \frac{\partial \breve{V}}{\partial T}\;. \tag{IV-42}$$

In a similar way carrying out the indicated differentiations in equation (IV-30) and making use of the change of variable theorem in partial differentiation one obtains

$$\frac{1}{T}\frac{\partial \breve{l}_p}{\partial T} - \frac{\breve{l}_p}{T^2} = \frac{1}{T}\frac{\partial \breve{c}_p}{\partial p}\;. \tag{IV-43}$$

Combining equations (IV-42) and (IV-43) one has

$$\breve{l}_p = -T\frac{\partial \breve{V}}{\partial T} \,. \tag{IV-44}$$

Carrying out the indicated differentiations in equation (IV-25) one has

$$\left(\frac{\partial\left(\frac{\partial U}{\partial m_1}\right)_{T,\,p,\,m_2}}{\partial T}\right)_{p,\,m_1,\,m_2} = (m_1 + m_2)\left[\left(\frac{\partial \breve{c}_p}{\partial m_1}\right)_{T,\,p,\,m_2} - p\left(\frac{\partial\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}}{\partial m_1}\right)_{T,\,p,\,m_2}\right] + \breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1} . \tag{IV-45}$$

Making use of equation (IV-14) one has

$$\left(\frac{\partial\left(\frac{\partial U}{\partial m_1}\right)_{T,\,p,\,m_2}}{\partial T}\right)_{p,\,m_1,\,m_2} = \left(\frac{\partial\left(\breve{U} + \breve{m}_2\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p}\right)}{\partial T}\right)_{p,\,m_1,\,m_2}$$

$$= \left(\frac{\partial \breve{U}}{\partial T}\right)_{p,\,m_1,\,m_2} + m_2\left(\frac{\partial\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p}}{\partial T}\right)_{p,\,m_1,\,m_2} . \tag{IV-46}$$

By application of the change of variable theorem in partial differentiation one then obtains

$$\left(\frac{\partial \breve{U}}{\partial T}\right)_{p,\, m_1,\, m_2} = \left(\frac{\partial \breve{U}}{\partial T}\right)_{p,\, \breve{m}_1} \left(\frac{\partial T}{\partial T}\right)_{p,\, m_1,\, m_2}$$

$$+ \left(\frac{\partial \breve{U}}{\partial p}\right)_{T,\, \breve{m}_1} \left(\frac{\partial p}{\partial T}\right)_{p,\, m_1,\, m_2} + \left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\, p} \left(\frac{\partial \breve{m}_1}{\partial T}\right)_{p,\, m_1,\, m_2} . \tag{IV-47}$$

The derivatives $\left(\frac{\partial p}{\partial T}\right)_{p,\, m_1,\, m_2}$ and $\left(\frac{\partial \breve{m}_1}{\partial T}\right)_{p,\, m_1,\, m_2}$ are each equal to zero. Thus one has

$$\left(\frac{\partial \breve{U}}{\partial T}\right)_{p,\, m_1,\, m_2} = \left(\frac{\partial \breve{U}}{\partial T}\right)_{p,\, \breve{m}_1} . \tag{IV-48}$$

Similarly it follows that

$$\left(\frac{\partial \left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\, p}}{\partial T}\right)_{p,\, m_1,\, m_2} = \left(\frac{\partial \left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\, p}}{\partial T}\right)_{p,\, \breve{m}_1} = \frac{\partial^2 \breve{U}}{\partial T \partial \breve{m}_1} . \tag{IV-49}$$

Also by application of the change of variable theorem in partial differentiation one obtains

$$\left(\frac{\partial \breve{c}_p}{\partial m_1}\right)_{T,\,p,\,m_2} = \left(\frac{\partial \breve{c}_p}{\partial T}\right)_{p,\,\breve{m}_1}\left(\frac{\partial T}{\partial m_1}\right)_{T,\,p,\,m_2} + \left(\frac{\partial \breve{c}_p}{\partial p}\right)_{T,\,\breve{m}_1}\left(\frac{\partial p}{\partial m_1}\right)_{T,\,p,\,m_2} + \left(\frac{\partial \breve{c}_p}{\partial \breve{m}_1}\right)_{T,\,p}\left(\frac{\partial \breve{m}}{\partial m_1}\right)_{T,\,p,\,m_2} .$$

(IV-50)

The two derivatives $\left(\frac{\partial T}{\partial m_1}\right)_{T,\,p,\,m_2}$ and $\left(\frac{\partial p}{\partial m_1}\right)_{T,\,p,\,m_2}$ are each equal to zero and the derivative $\left(\frac{\partial \breve{m}_1}{\partial m_1}\right)_{T,\,p,\,m_2}$ is equal to $\frac{\breve{m}_2}{m_1 + m_2}$. Thus we have

$$\left(\frac{\partial \breve{c}_p}{\partial m_1}\right)_{T,\,p,\,m_2} = \left(\frac{\partial \breve{c}_p}{\partial \breve{m}_1}\right)_{T,\,p} \frac{\breve{m}_2}{m_1 + m_2} . \qquad \text{(IV-51)}$$

Similarly we have

$$\left(\frac{\partial\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}}{\partial m_1}\right)_{T, p, m_2} = \left(\frac{\partial\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}}{\partial \breve{m}_1}\right)_{T, p} \frac{\breve{m}_2}{m_1 + m_2}$$

$$= \frac{\partial^2 \breve{V}}{\partial \breve{m}_1 \partial T} \frac{\breve{m}_2}{m_2 + m_2}. \qquad \text{(IV-52)}$$

Consequently substituting the values of the derivatives from the right side of equation (IV-46) for the value of the derivative on the left side of equation (IV-45) one obtains

$$\left(\frac{\partial \breve{U}}{\partial T}\right)_{p, m_1, m_2} + \breve{m}_2\left(\frac{\partial\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p}}{\partial T}\right)_{p, m_1, m_2}$$

$$= (m_1 + m_2)\left[\left(\frac{\partial \breve{c}_p}{\partial m_1}\right)_{T, p, m_2} - p\left(\frac{\partial\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}}{\partial m_1}\right)_{T, p, m_2}\right]$$

$$+ \breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}. \qquad \text{(IV-53)}$$

Next substituting the values of the derivatives from equations (IV-48), (IV-49), (IV-51), and (IV-52) in equation (IV-53) one has

$$\left(\frac{\partial \breve{U}}{\partial T}\right)_{p,\breve{m}_1} + \breve{m}_2 \frac{\partial^2 \breve{U}}{\partial T \partial \breve{m}_1}$$

$$= (m_1 + m_2)\left[\frac{\breve{m}_2}{m_1 + m_2}\left(\frac{\partial \breve{c}_p}{\partial \breve{m}_1}\right)_{T,p} - \frac{\breve{m}_2}{m_1 + m_2}\, p \,\frac{\partial^2 \breve{V}}{\partial \breve{m}_1 \partial T}\right]$$

$$+ \breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right) \quad \text{(IV-54)}$$

The derivative $\left(\frac{\partial \breve{U}}{\partial T}\right)_{p,\breve{m}_1}$ is equal to $\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}$.

Hence one obtains finally

$$\frac{\partial^2 \breve{U}}{\partial T \partial \breve{m}_1} = \frac{\partial \breve{c}_p}{\partial \breve{m}_1} - p\frac{\partial^2 \breve{V}}{\partial \breve{m}_1 \partial T}\,{}^{1} \quad \text{(IV-55)}$$

In a similar way carrying out the indicated differentiations in equation (IV-31) and making use of the change of variable theorem in partial differentiation one has

M: - i -ssf- • [2] (IV-56)

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[1] The same result is derivable from equation (I¥-26)..

[2] The same result is derivable from equation (IV-32).

Combining equations (IV-55) and (IV-56) one has

$$\frac{\partial^2\tilde{U}}{\partial T\partial\tilde{m}_1} = T\frac{\partial^2\tilde{S}}{\partial T\partial\tilde{m}_1} - p\frac{\partial^2\tilde{V}}{\partial T\partial\tilde{m}_1} \quad \text{(IV-57)}$$

Likewise carrying out the indicated differentiations in equation (IV-27) and making use of the change of variable theorem in partial differentiation one obtains

$$\frac{\partial^2\tilde{U}}{\partial p\partial\tilde{m}_1} = \frac{\partial\tilde{l}_p}{\partial\tilde{m}_1} - p\frac{\partial^2\tilde{V}}{\partial p\partial\tilde{m}_1} \text{ [3]} \quad \text{(IV-58)}$$

Also, carrying out the indicated differentiations in equation (IV-33) and making use of the change of variable theorem in partial differentiation one has

$$\frac{\partial^2\tilde{S}}{\partial p\partial\tilde{m}_1} = \frac{1}{T}\frac{\partial\tilde{l}_p}{\partial\tilde{m}_1} \text{ . [4]} \quad \text{(IV-59)}$$

Combining equations (IV-58) and (IV-59) one has

$$\frac{\partial^2\tilde{U}}{\partial p\partial\tilde{m}_1} = T\frac{\partial^2\tilde{S}}{\partial p\partial\tilde{m}_1} - p\frac{\partial^2\tilde{V}}{\partial p\partial\tilde{m}_1} \quad \text{(IV-60)}$$

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[3] The same result is derivable from equation (IV-28).

[4] The same result is derivable from equation (IV-34).

From (IV-44) it follows that

$$\frac{\partial \breve{l}_p}{\partial T} = -T\frac{\partial^2 \breve{V}}{\partial T^2} - \frac{\partial \breve{V}}{\partial T} \qquad \text{(IV-61)}$$

and from (IV-43), (IV-44) and (IV-61) it also follows that

$$\frac{\partial \breve{c}_p}{\partial p} = -T\frac{\partial^2 \breve{V}}{\partial T^2} \ . \qquad \text{(IV-62)}$$

From (IV-44) it follows that

$$\frac{\partial \breve{l}_p}{\partial p} = -T\frac{\partial^2 \breve{V}}{\partial p \partial T} \qquad \text{(IV-63)}$$

and

$$\frac{\partial \breve{l}_p}{\partial \breve{m}_1} = -T\frac{\partial^2 \breve{V}}{\partial \breve{m}_1 \partial T} \ . \qquad \text{(IV-64)}$$

Combining (IV-58) and (IV-64) one has

$$\frac{\text{[illegible]}}{\partial p \partial \breve{m}_1} = -T\frac{\text{[illegible]}}{\partial \breve{m}_1 \partial T} - p\frac{\text{[illegible]}}{\partial \breve{m}_1 \partial p} \qquad \text{(IV-65)}$$

and, similarly, combining (IV-59) and (IV-64) one has

$$\frac{\partial^2 \breve{S}}{\partial p \partial \breve{m}_1} = -\frac{\partial^2 \breve{V}}{\partial \breve{m}_1 \partial T} \ . \qquad \text{(IV-66)}$$

Finally substituting the value of l_p from equation (IV-44) in equations (IV-13) and (IV-21) one obtains

$$\left(\frac{\partial U}{\partial p}\right)_{T,\, m_1,\, m_2} = -(m_1 + m_2)\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1} + p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1}\right] \tag{IV-67}$$

and

$$\left(\frac{\partial S}{\partial p}\right)_{T,\, m_1,\, m_2} = -(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1} . \tag{IV-68}$$

Thus, just as in the case of a binary system of one phase and of unit mass, there is one relation, equation (IV-44), between the seven derivatives, $\frac{\partial \breve{V}}{\partial T}$, $\frac{\partial \breve{V}}{\partial p}$, $\frac{\partial \breve{V}}{\partial \breve{m}_1}$, $\breve{c}_p$, $\breve{l}_p$, $\frac{\partial \breve{U}}{\partial \breve{m}_1}$, $\frac{\partial \breve{S}}{\partial \breve{m}_1}$. Consequently all seven will be known if the following six are determined by means of experimental measurements: $\frac{\partial \breve{V}}{\partial T}$, $\frac{\partial \breve{V}}{\partial p}$, $\frac{\partial \breve{V}}{\partial \breve{m}_1}$, $\breve{c}_p$, $\frac{\partial \breve{U}}{\partial \breve{m}_1}$, $\frac{\partial \breve{S}}{\partial \breve{m}_1}$. There are also eight relations, equations (IV-55), (IV-56), (IV-61), (IV-62), (IV-63), (IV-64), (IV-65), (IV-66), between the eighteen derivatives, $\frac{\partial^2 \breve{V}}{\partial T^2}$, $\frac{\partial^2 \breve{V}}{\partial p^2}$, $\frac{\partial^2 \breve{V}}{\partial \breve{m}_1^2}$, $\frac{\partial^2 \breve{V}}{\partial T \partial p}$, $\frac{\partial^2 \breve{V}}{\partial T \partial \breve{m}_1}$, $\frac{\partial^2 \breve{V}}{\partial p \partial \breve{m}_1}$,

$\frac{\partial \breve{c}_p}{\partial T}$, $\frac{\partial \breve{c}_p}{\partial p}$, $\frac{\partial \breve{c}_p}{\partial \breve{m}_1}$, $\frac{\partial \breve{l}}{\partial T}$, $\frac{\partial \breve{l}}{\partial p}$, $\frac{\partial \breve{l}}{\partial \breve{m}_1}$, $\frac{\partial^2 \breve{V}}{\partial T \partial \breve{m}_1}$, $\frac{\partial^2 \breve{V}}{\partial p \partial \breve{m}_1}$, $\frac{\partial^2 \breve{U}}{\partial \breve{m}_1^2}$, $\frac{\partial^2 \breve{U}}{\partial T \partial \breve{m}_1}$, $\frac{\partial^2 \breve{U}}{\partial p \partial \breve{m}_1}$, $\frac{\partial^2 \breve{S}}{\partial \breve{m}_1^2}$, by means of which from the following ten,

$$\frac{\partial^2 \breve{V}}{\partial T^2}, \frac{\partial^2 \breve{V}}{\partial p^2}, \frac{\partial^2 \breve{V}}{\partial \breve{m}_1^2}, \frac{\partial^2 \breve{V}}{\partial T \partial p}, \frac{\partial^2 \breve{V}}{\partial T \partial \breve{m}_1}, \frac{\partial^2 \breve{V}}{\partial p \partial \breve{m}_1}, \frac{\partial \breve{c}_p}{\partial T}, \frac{\partial \breve{c}_p}{\partial \breve{m}_1}, \frac{\partial^2 \breve{U}}{\partial \breve{m}_1^2}, \frac{\partial^2 \breve{S}}{\partial \breve{m}_1^2},$$

the remaining eight can be calculated. From equation (IV-62) $\frac{\partial \breve{c}_p}{\partial p}$ can be calculated; from equation (IV-61) $\frac{\partial \breve{l}}{\partial T}$ can be calculated; from equation (IV-63) $\frac{\partial \breve{l}}{\partial p}$ can be calculated; from equation (IV-64) $\frac{\partial \breve{c}_p}{\partial \breve{m}_1}$ can be calculated; from equation (IV-55) $\frac{\partial^2 \breve{U}}{\partial T \partial \breve{m}_1}$ can be calculated; from equation (IV-55) $\frac{\partial^2 \breve{U}}{\partial p \partial \breve{m}_1}$ can be calculated; from equation (IV-56) $\frac{\partial^2 \breve{S}}{\partial T \partial \breve{m}_1}$ can be calculated; and from equation (IV-66) $\frac{\partial^2 \breve{S}}{\partial p \partial \breve{m}_1}$ can be calculated.

It will therefore suffice in the case of a binary system of one phase and of variable total mass, just as in the case of a binary system of one phase and of unit mass, to determine the specific volume over the range of temperature, pressure, and composition that is of interest. The value of $\breve{c}_p$ then needs to be determined as a function of temperature and composition at one pressure. Finally the values of the energy and the entropy need to be determined as functions of the composition at one temperature and one pressure. Thus in order to obtain complete therraodynamic information for a binary system of one phase and of variable total mass no additional experimental measurements have to be made beyond those required to be made in order to obtain complete thermodynamic information for a binary system of one phase and of unit mass over the same range of temperature, pressure, and composition. The necessary measurements to obtain complete thermodynamic information for a binary system of one phase and of unit mass over a given range of temperature, pressure, and composition were described in Part III of this text on pages 126-136. In part III the use of galvanic cells to determine the specific Gibbs function was explained, and from the specific Gibbs function combined with measurements of the specific volume and determinations of the specific energy (which do not require measurements of heat quantities under equilibrium conditions) the calculation of the specific entropy was also explained. In the author's article entitled "The Operational Basis and Mathematical Derivation of the Gibbs Differential Equation, Which Is the Fundamental Equation of Chemical Thermodynamics"[5] it was shown how osmotic cells could also be used in place of galvanic cells to obtain the specific Gibbs function.

It is notable that in order to obtain complete thermodynamic information for a binary system of one phase and of unit mass, and likewise for a binary system of one phase

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[5] Tunell, G., in *Thermodynamics of Minerals and Melts - Advances in Physical Geochemistry,* edited by R.C. Newton, A. Navrotsky, and 3.J. Wood, Springer-Verlag New York, Inc., New York, Heidelberg, Berlin, 1981, pp. 3-16.

and of variable total mass no definition or measurement of heat or work in the case of an open system when masses are being transferred to or from the system is required.[6]

Derivation of any desired relation between the thermodynamic quantities $T, p,$ mi, JH_2, V_9 U_9 $S,$ and their first derivatives for a binary system of one phase and of variable total mass by the use of functional determinants (Jacobians)

Equations (IV-1), (IV-11), and (IV-19) can, in general, be solved for any three of the quantities, T_9 $p,$ $m\backslash_9$ /T?$_2$» V_9 U_f $S,$ as functions of the remaining four. The first partial derivative of any one of the quantities, $T,$ p, mi» m_2> $V,$ U_9 S_9 with respect to any second quantity when any third, fourth, and fifth quantities are held constant can be obtained in terms of the six derivatives -^=, TT~, TTZ; * c_{nf} TTZ? , TTZ , 01 op oiB\ y dm i aw i

and certain of the quantities T, p, mi, m_2» $\breve{m}i$, $\breve{m}_2$^ $\breve{V}$, $\breve{U}_f$ $\breve{S}$, by application of the theorem stating that, if w' = OJ(V» $x, y, z)t$ w = $f(s, t_9 u, v)_9$ x = <p(s_9 t, u, $v)_f$ y = ^(s, t, u, v), z = $6(Si$» t, u, v), then one has

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[6] The definitions of heat and work in the case of open systems used by various authors are discussed in Appendix A to Part II and Appendix A to Part IV of this text.

$$\left(\frac{\partial w'}{\partial w}\right)_{x,\,y,\,z} = \frac{\begin{vmatrix} \frac{\partial w'}{\partial s} & \frac{\partial w'}{\partial t} & \frac{\partial w'}{\partial u} & \frac{\partial w'}{\partial v} \\ \frac{\partial x}{\partial s} & \frac{\partial x}{\partial t} & \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} \\ \frac{\partial y}{\partial s} & \frac{\partial y}{\partial t} & \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} \\ \frac{\partial z}{\partial s} & \frac{\partial z}{\partial t} & \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} \end{vmatrix}}{\begin{vmatrix} \frac{\partial w}{\partial s} & \frac{\partial w}{\partial t} & \frac{\partial w}{\partial u} & \frac{\partial w}{\partial v} \\ \frac{\partial x}{\partial s} & \frac{\partial x}{\partial t} & \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} \\ \frac{\partial y}{\partial s} & \frac{\partial y}{\partial t} & \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} \\ \frac{\partial z}{\partial s} & \frac{\partial z}{\partial t} & \frac{\partial z}{\partial u} & \frac{\partial z}{\partial v} \end{vmatrix}} = \frac{\dfrac{\partial(w', x, y, z)}{\partial(s, t, u, v)}}{\dfrac{\partial(w, x, y, z)}{\partial(s, t, u, v)}} , \qquad \text{(IV-69)}$$

provided all the partial derivatives are continuous and provided the determinant in the denominator is not equal to zero.

In Tables IV-1 to IV-35 (on pages 230-264) the value of the Jacobian is given for each set of four of the variables, T, p, m_1, m_2, V, U, S as w', x, y, z or w, x, y, z, and with T, p, m_1, m_2 as s, t, u, v. There are 140 Jacobians in the Tables, but one has

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

(IV-70), (IV-71), (IV-72)

because interchanging two rows of a determinant changes the sign of the determinant. Hence it is only necessary to calculate the values of 35 of the 140 Jacobians. The calculations of these 35 Jacobians follow:

$$\frac{\partial(m_2, T, p, m_1)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial m_2}{\partial T} \cdot 0 - \frac{\partial m_2}{\partial p} \cdot 0 + \frac{\partial m_2}{\partial m_1} \cdot 0 - \frac{\partial m_2}{\partial m_2} \cdot 1$$

$$= 0 - 0 + 0 - 1 \cdot 1$$

$$= -1 \; ; \qquad \text{(IV-73)}$$

$$\frac{\partial(V, T, p, m_1)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial V}{\partial T} \cdot 0 - \frac{\partial V}{\partial p} \cdot 0 + \frac{\partial V}{\partial m_1} \cdot 0 - \frac{\partial V}{\partial m_2} \cdot 1$$

$$= -\frac{\partial V}{\partial m_2}$$

$$= -\breve{V} + \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} ; \qquad \text{(IV-74)}$$

$$\frac{\partial(U, T, p, m_1)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial U}{\partial T} \cdot 0 - \frac{\partial U}{\partial p} \cdot 0 + \frac{\partial U}{\partial m_1} \cdot 0 - \frac{\partial U}{\partial m_2}$$

$$= -\frac{\partial U}{\partial m_2}$$

$$= -\breve{U} + \breve{m}_1\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} ; \qquad \text{(IV-75)}$$

$$\frac{\partial(\breve{S}, T, p, \breve{m}_1)}{\partial(T, p, \breve{m}_1, \breve{m}_2)} = \begin{vmatrix} \frac{\partial \breve{S}}{\partial T} & \frac{\partial \breve{S}}{\partial p} & \frac{\partial \breve{S}}{\partial \breve{m}_1} & \frac{\partial \breve{S}}{\partial \breve{m}_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial \breve{m}_1} & \frac{\partial T}{\partial \breve{m}_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial \breve{m}_1} & \frac{\partial p}{\partial \breve{m}_2} \\ \frac{\partial \breve{m}_1}{\partial T} & \frac{\partial \breve{m}_1}{\partial p} & \frac{\partial \breve{m}_1}{\partial \breve{m}_1} & \frac{\partial \breve{m}_1}{\partial \breve{m}_2} \end{vmatrix}$$

$$= \frac{\partial \breve{S}}{\partial T} \cdot 0 - \frac{\partial \breve{S}}{\partial p} \cdot 0 + \frac{\partial \breve{S}}{\partial \breve{m}_1} \cdot 0 - \frac{\partial \breve{S}}{\partial \breve{m}_2} \cdot 1$$

$$= -\frac{\partial \breve{S}}{\partial \breve{m}_2}$$

$$= -\breve{S} + \breve{m}_1 \left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\, p} ; \qquad \text{(IV-76)}$$

$$\frac{\partial(V, r, p, m_2)}{\partial(r, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial V}{\partial r} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \\ \frac{\partial r}{\partial r} & \frac{\partial r}{\partial p} & \frac{\partial r}{\partial m_1} & \frac{\partial r}{\partial m_2} \\ \frac{\partial p}{\partial r} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_2}{\partial r} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial V}{\partial r} \cdot 0 - \frac{\partial V}{\partial p} \cdot 0 + \frac{\partial V}{\partial m_1} \qquad \frac{\partial V}{\partial m_2}$$

$$= \frac{\partial V}{\partial m_1}$$

$$= \breve{V} + \breve{m}_2 \left(\frac{\partial \breve{V}}{\partial \breve{m}}\right)_{r,\,p}, \qquad \text{(IV-77)}$$

$$\frac{\partial(U,\ T,\ p,\ m_2)}{\partial(T,\ p,\ m_1,\ m_2)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial U}{\partial T} \cdot 0 - \frac{\partial U}{\partial p} \cdot 0 + \frac{\partial U}{\partial m_1} \cdot 1 - \frac{\partial U}{\partial m_2} \cdot 0$$

$$= \frac{\partial U}{\partial m_1}$$

$$= \breve{U} + \breve{m}_2 \left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\ p} ; \qquad \text{(IV-78)}$$

$$\frac{\partial(S, T, p, m_2)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T} \cdot 0 - \frac{\partial S}{\partial p} \cdot 0 + \frac{\partial S}{\partial m_1} \cdot 1 - \frac{\partial S}{\partial m_2} \cdot 0$$

$$= \frac{\partial S}{\partial m_1}$$

$$= \check{S} + s_2 \left(\frac{4}{\partial m_1}\right)_{T, p} ; \qquad \text{(IV-79)}$$

$$\frac{\partial(U, T, p, V)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial U}{\partial T} \cdot 0 - \frac{\partial U}{\partial p} \cdot 0 + \frac{\partial U}{\partial m_1} \cdot \frac{\partial V}{\partial m_2} - \frac{\partial U}{\partial m_2} \cdot \frac{\partial V}{\partial m_1}$$

$$= \frac{\partial U}{\partial m_1} \frac{\partial V}{\partial m_2} - \frac{\partial U}{\partial m_2} \cdot \frac{\partial V}{\partial m_1}$$

$$= -\breve{U}\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p} + \breve{V}\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} ; \qquad \text{(IV-80)}$$

$$\frac{\partial(S,\ T,\ p,\ V)}{\partial(T,\ p,\ m_1,\ m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T}\,\cdots\,\frac{\partial S}{\partial p}\,\cdots\,\frac{\partial S}{\partial m_1}\,\frac{\partial F}{\partial m_2}\,\cdot\,\frac{\partial S}{\partial m_2}\,\frac{\partial V}{\partial m_1}$$

$$= \frac{\partial S}{\partial m_1}\,\frac{\partial V}{\partial m_2} - \frac{\partial S}{\partial m_2}\,\frac{\partial V}{\partial m_1}$$

$$= -\breve{S}\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p} + \breve{V}\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p}\ ; \qquad \text{(IV-81)}$$

$$\frac{\partial(S, T, p, U)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \end{vmatrix}$$

$$= \quad dT \qquad dp \cdot 0 + dm_1 \;\; dm_2 \;\; dm_2 \;\; \partial m_1$$

$$= \frac{\partial S}{\partial m_1} \cdot \frac{\partial U}{\partial m_2} - \frac{\partial S}{\partial m_2} \cdot \frac{\partial U}{\partial m_1}$$

$$= -\bar{S}\left(\frac{\partial \bar{U}}{\partial \bar{m}_1}\right)_{T,p} + \bar{U}\left(\frac{\partial \bar{S}}{\partial \bar{m}_1}\right)_{T,p}; \qquad \text{(IV-82)}$$

$$\frac{\partial(V, T, m_1, m_2)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \end{vmatrix}$$

$$= \quad \frac{\partial V}{\partial T} \qquad \frac{\partial V}{\partial p} \qquad \frac{\partial V}{\partial m_1} \qquad \frac{\partial V}{\partial m_2}$$

$$= - \frac{\partial V}{\partial p}$$

$$= - (m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1}; \tag{IV-83}$$

$$\frac{\partial(U, T, m_1, m_2)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial U}{\partial T} \cdot 0 - \frac{\partial U}{\partial p} \cdot 1 + \frac{\partial U}{\partial m_1} \cdot 0 - \frac{\partial U}{\partial m_2} \cdot 0$$

$$= -\frac{\partial U}{\partial p}$$

$$= (m_1 + m_2)\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1} + p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right]; \quad \text{(IV-84)}$$

$$
\frac{\partial(S, T, m_1, m_2)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix}
\frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\
\frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\
\frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\
\frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2}
\end{vmatrix}
$$

$$
= \frac{\partial S}{\partial T} \cdot 0 - \frac{\partial S}{\partial p} \cdot 1 + \frac{\partial S}{\partial m_1} \cdot 0 - \frac{\partial S}{\partial m_2} \cdot 0
$$

$$
= -\frac{\partial S}{\partial p}
$$

$$
= (m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}; \qquad \text{(IV-85)}
$$

$$\frac{\partial(U, T, m_1, V)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial U}{\partial T} \cdot 0 - \frac{\partial U}{\partial p} \cdot \frac{\partial V}{\partial m_2} + \frac{\partial U}{\partial m_1} \cdot 0 + \frac{\partial U}{\partial m_2} \cdot \frac{\partial V}{\partial p}$$

$$= -\frac{\partial U}{\partial p} \cdot \frac{\partial V}{\partial m_2} + \frac{\partial U}{\partial m_1} \cdot \frac{\partial V}{\partial p}$$

$$= (m_1 + m_2)\left\{\left[(\breve{U} + p\breve{V}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}\right)\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right.$$

$$\left. + \left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}\right] T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}\right\}; \qquad \text{(IV-86)}$$

$$\frac{\partial(S,\ T,\ m_1,\ V)}{\partial(T,\ p,\ m_1,\ m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T} \cdot 0 - \frac{\partial S}{\partial p} \cdot \frac{\partial V}{\partial m_2} + \frac{\partial S}{\partial m_1} \cdot 0 + \frac{\partial S}{\partial m_2} \cdot \frac{\partial V}{\partial p}$$

$$= -\frac{\partial S}{\partial p} \quad \partial m_2 \quad \partial m_1 \quad \partial p$$

$$= (m_1 + m_2)\left\{\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\ p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\ \breve{m}_1}\right.$$

$$\left. + \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\ p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\ \breve{m}_1}\right\} \;; \qquad \text{(IV-87)}$$

$$\frac{\partial(S,\ T,\ m_1,\ U)}{\partial(T,\ p,\ m_1,\ m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \end{vmatrix}$$

= dT dp dm2 dm1 dm2 dp

$$= -\frac{\partial S}{\partial p}\cdot\frac{\partial U}{\partial m_2} + \frac{\partial U}{\partial m_2}\cdot\frac{\partial S}{\partial p}$$

$$= (m_1 + m_2)\left\{\left[(\breve{U} - T\breve{S}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\ p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\ p}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\ \breve{m}_1}\right.$$

$$\left. - \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\ p}\right]p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\ \breve{m}_1}\right\} ; \qquad \text{(IV-88)}$$

$$\frac{\partial(U, T, m_2, V)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial V}{\partial T}\cdot 0 + \frac{\partial U}{\partial p}\cdot\frac{\partial V}{\partial m_1} - \frac{\partial U}{\partial m_1}\frac{\partial V}{\partial p} - \frac{\partial U}{\partial m_2}\cdot 0$$

$$= \frac{\partial U}{\partial p}\cdot\frac{\partial V}{\partial m_1} - \frac{\partial U}{\partial m_1}\cdot\frac{\partial V}{\partial p}$$

$$= -(m_1 + m_2)\left\{\left[(\breve{U} + p\breve{V}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right.$$

$$\left. + \left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right] T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\right\}; \qquad \text{(IV-89)}$$

$$\frac{\partial(S, T, m_2, V)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T} \cdot 0 + \frac{\partial S}{\partial p} \cdot \frac{\partial V}{\partial m_1} - \frac{\partial S}{\partial m_1} \cdot \frac{\partial V}{\partial p} - \frac{\partial S}{\partial m_2} \cdot 0$$

$$= \frac{\partial S}{\partial p} \cdot \frac{\partial V}{\partial m_1} - \frac{\partial S}{\partial m_1} \cdot \frac{\partial V}{\partial p}$$

$$= -(m_1 + m_2)\left\{\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} + \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right\}. \qquad \text{(IV-90)}$$

$$\frac{\partial(S, T, m_2, U)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T}\cdot 0 + \frac{\partial S}{\partial p}\,\frac{\partial T}{\partial m_1} - \frac{\partial S}{\partial m_1}\,\frac{\partial U}{\partial p} - \frac{\partial S}{\partial m_2}\, 0$$

$$= \frac{\partial S}{\partial p}\cdot\frac{\partial}{\partial m_1} \quad \frac{\partial S}{\partial m_1}\,\frac{\partial U}{\partial p}$$

$$= -(m_1 + m_2)\left\{\left[(\breve{U} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}\right.$$

$$\left. - \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p}\right] p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right\}\ ; \qquad \text{(IV-91)}$$

$$\frac{\partial(S, T, V, U)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T} \cdot 0 - \frac{\partial S}{\partial p}\left(\frac{\partial V}{\partial m_1} \cdot \frac{\partial U}{\partial m_2} - \frac{\partial U}{\partial m_1} \cdot \frac{\partial V}{\partial m_2}\right)$$

$$+ \frac{\partial S}{\partial m_1}\left(\frac{\partial V}{\partial p} \cdot \frac{\partial U}{\partial m_2} - \frac{\partial U}{\partial p} \cdot \frac{\partial V}{\partial m_2}\right)$$

$$- \frac{\partial S}{\partial m_2}\left(\frac{\partial V}{\partial p} \cdot \frac{\partial U}{\partial m_1} - \frac{\partial U}{\partial p} \cdot \frac{\partial V}{\partial m_1}\right)$$

$$= (m_1 + m_2)\left\{\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} - \breve{V}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right)\right]\right.$$

$$\left. + \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p} - \breve{S}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right)\right]\right\};$$

(IV-92)

$$\frac{\partial(V, p, m_1, m_2)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial V}{\partial T} \cdot 1 - \frac{\partial V}{\partial p} \cdot 0 + \frac{\partial V}{\partial m_1} \cdot 0 - \frac{\partial V}{\partial m_2} \cdot 0$$

$$= \frac{\partial V}{\partial T}$$

$$= (m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\ \breve{m}_1} ; \qquad \text{(IV-93)}$$

$$\frac{\partial(U, p, m_1, m_2)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial U}{\partial T} \cdot 1 - \frac{\partial U}{\partial p} \times 0 + \frac{\partial U}{\partial m_1} \cdot 0 - \frac{\partial U}{\partial m_2} \cdot 0$$

$$= \frac{\partial U}{\partial T}$$

$$= (m_1 + m_2)\left[c_p - p\left(\frac{\partial v}{\partial T}\right)_{p,\, m_1}\right]; \qquad \text{(IV-94)}$$

$$\frac{\partial(S, p, m_1, m_2)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \end{vmatrix}$$

= <3i dp dm i dm 2

$$= \frac{\partial S}{\partial T}$$

$$= (m_1 + m_2) \frac{c_p}{T} \quad ; \qquad \text{(IV-95)}$$

$$\frac{\partial(U,\ p,\ m_1,\ V)}{\partial(T,\ p,\ m_1,\ m_2)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial U}{\partial T}\cdot\frac{\partial V}{\partial m_2} - \frac{\partial U}{\partial p}\cdot 0 + \frac{\partial U}{\partial m_1}\cdot 0 - \frac{\partial U}{\partial m_2}\cdot\frac{\partial V}{\partial T}$$

$$= \frac{\partial U}{\partial T}\cdot\frac{\partial V}{\partial m_2} - \frac{\partial U}{\partial m_2}\cdot\frac{\partial V}{\partial T}$$

$$= -(m_1 + m_2)\left\{\left[(\breve{U} + p\breve{V}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\ p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\ p}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\ \breve{m}_1}\right.$$

$$\left. - \breve{C}_p\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\ p}\right]\right\}; \qquad \text{(IV-96)}$$

$$\frac{\partial(S,\ p,\ m_1,\ V)}{\partial(T,\ p,\ m_1,\ m_2)} = \begin{vmatrix} \dfrac{\partial S}{\partial T} & \dfrac{\partial S}{\partial p} & \dfrac{\partial S}{\partial m_1} & \dfrac{\partial S}{\partial m_2} \\[2ex] \dfrac{\partial p}{\partial T} & \dfrac{\partial p}{\partial p} & \dfrac{\partial p}{\partial m_1} & \dfrac{\partial p}{\partial m_2} \\[2ex] \dfrac{\partial m_1}{\partial T} & \dfrac{\partial m_1}{\partial p} & \dfrac{\partial m_1}{\partial m_1} & \dfrac{\partial m_1}{\partial m_2} \\[2ex] \dfrac{\partial V}{\partial T} & \dfrac{\partial V}{\partial p} & \dfrac{\partial V}{\partial m_1} & \dfrac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T} \cdot \frac{\partial V}{\partial m_2} - \frac{\partial S}{\partial p} \cdot 0 + \frac{\partial S}{\partial m_1} \cdot 0 - \frac{\partial S}{\partial m_2} \cdot \frac{\partial V}{\partial T}$$

$$= \frac{\partial S}{\partial T} \cdot \frac{\partial V}{\partial m_2} - \frac{\partial S}{\partial m_2} \cdot \frac{\partial V}{\partial T}$$

$$= (m_1 + m_2)\left\{\frac{\breve{c}_p}{T}\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\ p}\right] - \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\ p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\ \breve{m}_1}\right\} ; \qquad \text{(IV-97)}$$

$$\frac{\partial(S, p, m_1, U)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T} \cdot \frac{\partial U}{\partial m_2} - \frac{\partial S}{\partial p} \cdot 0 + \frac{\partial S}{\partial m_1} \cdot 0 - \frac{\partial S}{\partial m_2} \frac{\partial U}{\partial T}$$

$$= \frac{\partial S}{\partial T} \cdot \frac{\partial U}{\partial m_2} - \frac{\partial S}{\partial m_2} \cdot \frac{\partial U}{\partial T}$$

$$= (\breve{m}_1 \text{[illegible]} \Big\{ \Big[\text{[illegible]} - T\breve{S}) - \breve{m}_1 \Big(\Big(\frac{\partial \breve{U}}{\partial \breve{m}_1} \Big)_{T,\,p} - T \Big(\frac{\partial \breve{S}}{\partial \breve{m}_1} \Big)_{T,\,p} \Big) \Big]$$

$$+ \Big[\breve{S} - \breve{m}_1 \Big(\frac{\partial \breve{S}}{\partial \breve{m}_1} \Big)_{T,\,p} \Big] p \Big(\frac{\partial \breve{V}}{\partial T} \Big)_{p,\,\breve{m}_1} \Big\} \quad ; \qquad \text{(IV-98)}$$

$$\frac{\partial(U,\ p,\ m_2,\ V)}{\partial(T,\ p,\ m_1,\ m_2)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= -\frac{\partial U}{\partial T}\cdot\frac{\partial V}{\partial m_1} - \frac{\partial U}{\partial p}\cdot 0 + \frac{\partial U}{\partial m_1}\cdot\frac{\partial V}{\partial T} - \frac{\partial U}{\partial m_2}\cdot 0$$

$$= -\frac{\partial U}{\partial T}\cdot\frac{\partial V}{\partial m_1} + \frac{\partial U}{\partial m_1}\cdot\frac{\partial V}{\partial T}$$

$$= (m_1 + m_2)\left\{\left[(\breve{U} + p\breve{V}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\ p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\ p}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\ \breve{m}_1}\right.$$

$$\left. - \breve{C}_p\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\ p}\right]\right\} ; \qquad \text{(IV-99)}$$

$$\frac{\partial(S,\ p,\ m_2,\ V)}{\partial(T,\ p,\ m_1,\ m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= -\frac{\partial S}{\partial T}\cdot\frac{\partial V}{\partial m_1} - \frac{\partial S}{\partial p}\cdot 0 + \frac{\partial S}{\partial m_1}\cdot\frac{\partial V}{\partial T} - \frac{\partial S}{\partial m_2}\cdot 0$$

$$= -\frac{\partial S}{\partial T}\cdot\frac{\partial V}{\partial m_1} + \frac{\partial S}{\partial m_1}\cdot\frac{\partial V}{\partial T}$$

$$= -(m_1 + m_2)\left\{\frac{\breve{C}_p}{T}\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\ p}\right]\right.$$

$$\left. - \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\ p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\ \breve{m}_1}\right\} ; \qquad \text{(IV-100)}$$

$$\frac{\partial(S,\ p,\ m_2,\ U)}{\partial(T,\ p,\ m_1,\ m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \end{vmatrix}$$

$$= -\frac{\partial S}{\partial T}\cdot\frac{\partial U}{\partial m_1} - \frac{\partial S}{\partial p}\cdot 0 + \frac{\partial S}{\partial m_1}\cdot\frac{\partial U}{\partial T} - \frac{\partial S}{\partial m_2}\cdot 0$$

$$= -\frac{\partial S}{\partial T}\cdot\frac{\partial U}{\partial m_1} + \frac{\partial S}{\partial m_1}\cdot\frac{\partial U}{\partial T}$$

$$= -(m_1 + m_2)\left\{\frac{\breve{C}_p}{T}\left[(\breve{U} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\ p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\ p}\right)\right]\right.$$

$$\left. + \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\ p}\right] p \left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\ \breve{m}_1}\right\} ; \qquad \text{(IV-101)}$$

$$\frac{\partial(S, p, V, U)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial p} & \frac{\partial p}{\partial m_1} & \frac{\partial p}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T}\left(\frac{\partial V}{\partial m_1} \cdot \frac{\partial U}{\partial m_2} - \frac{\partial U}{\partial m_1} \cdot \frac{\partial V}{\partial m_2}\right) - \frac{\partial S}{\partial p} \cdot 0$$

$$+ \frac{\partial S}{\partial m_1}\left(\frac{\partial V}{\partial m_2} \cdot \frac{\partial U}{\partial T} - \frac{\partial V}{\partial T} \cdot \frac{\partial U}{\partial m_2}\right)$$

$$- \frac{\partial S}{\partial m_2}\left(\frac{\partial V}{\partial m_1} \cdot \frac{\partial U}{\partial T} - \frac{\partial V}{\partial T} \cdot \frac{\partial U}{\partial m_1}\right)$$

$$(m_1 + m_2)\left\{\frac{\breve{c}_p}{T}\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p} - \breve{V}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p}\right)\right]\right.$$

$$\left. - \left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p} - \breve{S}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}\right)\right]\right\};$$

(IV-102)

$$\frac{\partial(U, m_1, m_2, V)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial U}{\partial T}\frac{\partial V}{\partial p} - \frac{\partial U}{\partial p}\frac{\partial V}{\partial T} + \frac{\partial U}{\partial m_1}\cdot 0 - \frac{\partial U}{\partial m_2}\cdot 0$$

$$= \frac{\partial U}{\partial T}\frac{\partial V}{\partial p} - \frac{\partial U}{\partial p}\frac{\partial V}{\partial T}$$

$$= (m_1 + m_2)^2\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\,\breve{m}_1} + \breve{c}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right] ; \qquad \text{(IV-103)}$$

$$\frac{\partial(S, m_1, m_2, V)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T}\frac{\partial V}{\partial p} - \frac{\partial S}{\partial p}\frac{\partial V}{\partial T} + \frac{\partial S}{\partial m_1}\, 0 - \frac{\partial S}{\partial m_2}\, 0$$

$$= (m_1 + m_2)^2\left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} + \frac{\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right] ; \qquad \text{(IV-104)}$$

$$\frac{\partial(S, m_1, m_2, U)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T} \cdot \frac{\partial U}{\partial p} - \frac{\partial S}{\partial p} \cdot \frac{\partial U}{\partial T} + \frac{\partial S}{\partial m_1} \cdot 0 - \frac{\partial S}{\partial m_2} \cdot 0$$

$$= -(m_1 + m_2)^2 \left[p \left(\frac{\partial \breve{V}}{\partial T} \right)^2_{p, \breve{m}_1} + \frac{p \breve{c}_p}{T} \left(\frac{\partial \breve{V}}{\partial p} \right)_{T, \breve{m}_1} \right] \quad ; \qquad \text{(IV-105)}$$

$$\frac{\partial(S, m_1, V, U)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T}\left(\frac{\partial U}{\partial m_2}\cdot\frac{\partial V}{\partial p} - \frac{\partial U}{\partial p}\cdot\frac{\partial V}{\partial m_2}\right)$$

$$- \frac{\partial S}{\partial p}\left(\frac{\partial U}{\partial m_2}\cdot\frac{\partial V}{\partial T} - \frac{\partial U}{\partial T}\cdot\frac{\partial V}{\partial m_2}\right) + \frac{\partial S}{\partial m_1}\cdot 0$$

$$- \frac{\partial S}{\partial m_2}\left(\frac{\partial U}{\partial p}\cdot\frac{\partial V}{\partial T} - \frac{\partial V}{\partial p}\cdot\frac{\partial U}{\partial T}\right)$$

$$= -(m_1 + m_2)^2\left\{\left[(\breve{U} + p\breve{V} - T\breve{S}) - \left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]\right.$$

$$\left.\cdot\left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} + \frac{\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right]\right\}; \qquad \text{(IV-106)}$$

$$\frac{\partial(S, m_2, V, U)}{\partial(T, p, m_1, m_2)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial p} & \frac{\partial S}{\partial m_1} & \frac{\partial S}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \\ \frac{\partial U}{\partial T} & \frac{\partial U}{\partial p} & \frac{\partial U}{\partial m_1} & \frac{\partial U}{\partial m_2} \end{vmatrix}$$

$$= \frac{\partial S}{\partial T}\left(\frac{\partial V}{\partial m_1}\frac{\partial U}{\partial p} - \frac{\partial U}{\partial m_1}\frac{\partial V}{\partial p}\right)$$

$$- \frac{\partial S}{\partial p}\left(\frac{\partial V}{\partial m_1}\frac{\partial U}{\partial T} - \frac{\partial U}{\partial m_1}\frac{\partial V}{\partial T}\right)$$

$$+ \frac{\partial S}{\partial m_1}\left(\frac{\partial V}{\partial p}\frac{\partial U}{\partial T} - \frac{\partial U}{\partial p}\frac{\partial V}{\partial T}\right) - \frac{\partial S}{\partial m_2}\cdot 0$$

$$= (m_1 + m_2)^2\left\{\left[(\breve{U} + p\breve{V} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial\breve{U}}{\partial\breve{m}_1}\right)_{T,p} + p\left(\frac{\partial\breve{V}}{\partial\breve{m}_1}\right)_{T,p} - T\left(\frac{\partial\breve{S}}{\partial\breve{m}_1}\right)_{T,p}\right)\right]\right.$$

$$\left.\cdot\left[\left(\frac{\partial\breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} + \frac{\breve{c}_p}{T}\left(\frac{\partial\breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right]\right\}. \qquad \text{(IV-107)}$$

Table IV-1
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)} * \frac{\partial(w, x, y, z)}{\partial(T, p, \bar{m}_1, \bar{m}_2)}$$

w \ x, y, z	T, p, m_1
m_2	-1
V	$-\bar{V} + \bar{m}_1\left(\frac{\partial \bar{V}}{\partial \bar{m}_1}\right)_{T,p}$
U	$-\bar{U} + \bar{m}_1\left(\frac{\partial \bar{U}}{\partial \bar{m}_1}\right)_{T,p}$
S	$-\bar{S} + \bar{m}_1\left(\frac{\partial \bar{S}}{\partial \bar{m}_1}\right)_{T,p}$

Table IV-2
Jacobians of extensive functions for a
binary system of one phase

$\dfrac{d(w', x, y, z)}{O\backslash l\ f\ P1\ Ul\backslash i\ \bar{U}12)}$ $\dfrac{d(w, x, y, z)}{\theta\{i\ \$\ pi\ ElI\ f\ 1112\ )}$

\>r, y, z w\ w \	Ttp, m_2
m_1	1
V	$\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\, p}$
U	$\breve{U} + \breve{m}_2\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\, p}$
5	$\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\, p}$

Table IV-3
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w,x,y,z)}{\partial(T,p,m_1,m_2)}\ ,\quad \frac{\partial(w,x,y,z)}{\partial(T,p,m_1,m_2)}$$

x, y, z / w	T, p, V
m_1	$\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}$
m_2	$-\breve{V} - \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}$
U	$-\breve{U}\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} + \breve{V}\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p}$
S	$-\breve{S}\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} + \breve{V}\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}$

Table IV-4
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)} = \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

w' \ x, y, z	$T, p, \tilde{U}$
m_1	[illegible] $\left(\frac{\partial \tilde{U}}{\partial \tilde{m}_1}\right)_{T,p}$
m_2	$-\left(\tilde{U} - m_2 \text{[illegible]}\right)$
V	$\tilde{U}\left(\frac{\partial \tilde{V}}{\partial \tilde{m}_1}\right)_{T,p} - \tilde{V}\left(\frac{\partial \tilde{U}}{\partial \tilde{m}_1}\right)_{T,p}$
S	$-\tilde{S}\left(\frac{\partial \tilde{U}}{\partial \tilde{m}_1}\right)_{T,p} + \tilde{U}\left(\frac{\partial \tilde{S}}{\partial \tilde{m}_1}\right)_{T,p}$

Table IV-5
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(v, x, y, z)}{\partial(T, p, m_1, m_2)}$$

w \ x, y, z	T, p, S
m_1	$\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}$
m_2	$-\breve{S} - \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}$
V	$\breve{S}\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - \breve{V}\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}$
U	$\breve{S}\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} - \breve{U}\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}$

Table IV-5
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

x, y, z / w', w	T, m_1, m_2
p	-1
V	$-(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$
U	$(m_1 + m_2)\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} + p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right]$
S	$(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}$

Table IV-7
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

w \ x, y, z	$T, \breve{m}_1, V$
p	$-\breve{V} + \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}$
[illegible]	$(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}$
V	[illegible] $\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\Big)\Big]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}$ $+ \left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right] T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\Big\}$
S	$(m_1 + m_2)\Big\{\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)$ [illegible] $+ \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\Big\}$

Table IV-8
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w', x, y, z)}{\partial(T, p, \tilde{m}_1, \tilde{m}_2)}$$

x, y, z / w', x	$T, \tilde{m}_1, \tilde{U}$
p	$-\tilde{U} + \tilde{m}_1\left(\frac{\partial \tilde{U}}{\partial \tilde{m}_1}\right)_{T, p}$
^2	$-(m_1 + m_2)\left[T\left(\frac{\partial \tilde{V}}{\partial T}\right)_{p, \tilde{m}_1} + p\left(\frac{\partial \tilde{V}}{\partial p}\right)_{T, \tilde{m}_1}\right]$
>	-(mi + i33₂)[(£1 + pV̆) - m̆ .//3f̆f \ /'®.)r.J(«l.Sl }
S	(mi + ffl₂)s[(L̆f - fe) - a•<(Ĭ,)T, p -nwr(Pjjujp>ffi - KsJ̆T .r, ˘aj

Table IV-9
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(x,\, y,\, z)}{\partial(T,\, p,\, m_1,\, m_2)}, \qquad \frac{\partial(x,\, y,\, z)}{\partial(T,\, p,\, \breve{m}_1,\, m_2)}$$

x, y, z	T, m_1, S
P	$-\breve{S} + \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\, p}$
[illegible]	$-(m_1 + m_2)\left(\frac{\partial V}{\partial T}\right)_{p,\, \breve{m}_1}$
V	$-(m_1 + m_2)\left\{\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\, p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1} - \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\, p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1}\right\}$
U	$-(m_1 + m_2)\left\{\left[(\breve{U} - T\breve{S}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\, p}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1} - \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\, p}\right]p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1}\right\}$

Table IV-10
Jacobians of extensive functions for a binary system of one phase

$\frac{\partial(w, x, y, z)}{\partial([illegible])}$, $\frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$

w \ x, y, z	T, m_2, V
p	[illegible]
V	$-(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$
U	[illegible] $+ p\breve{V}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,}$ [illegible] $+ \left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right] T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} \Big\}$
S	$-(m_1 + m_2)\Big\{\Big[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,}$ [illegible] $\Big]$ [illegible] $+ \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1} \Big\}$

Table IV-11
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

x, y, z / w', w	T, m_2, U
P	$\breve{U} + \breve{m}_2\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p}$
·,	$(m_1 + m_2)\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} + p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right]$
V	$(m_1 + m_2)\left\{\left[(\breve{U} + p\breve{V}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right)\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1} + \left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\right\}$
>	[illegible] $- T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right)\Big]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}$ [illegible] $-\left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right]p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\Big\}$

Table IV-12 Jacobians of extensive functions for a binary system of one phase	
$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}$, $\frac{\partial(w, x, y, z)}{\partial(T, p, \breve{m}_1, m_2)}$	
x, y, z / w', w	T, m_2, S
P	$\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}$
«	$(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}$
V	$(m_1 + m_2)\left\{\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right]$ [illegible] $+ \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right\}$
•	[illegible] $T\breve{S}$ [illegible] $- T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\Big)\Big]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}$ [illegible] $_{,\breve{m}_1}\Big\}$

Table IV-13
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

x, y, z / w', w	T, V, U
p	$-\breve{U}\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} + \breve{V}\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p}$
m_1	$(m_1 + m_2)\left\{\left[(\breve{U} + p\breve{V}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right.$ [illegible]
[illegible]	[illegible]
S	$(m_1 + m_2)\left\{\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - \breve{V}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\right.$ [illegible]

Table IV-14 Jacobians of extensive functions for a binary system of one phase	
$\dfrac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}$, $\dfrac{\partial(w, x, y, z)}{\partial(T, p, \breve{m}_1, m_2)}$	
x, y, z / w	T, V, S
p	$-\breve{S}\left(\dfrac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} + \breve{V}\left(\dfrac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}$
m_1	$(m_1 + m_2)\left\{\left[\breve{V} - \breve{m}_1\left(\dfrac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\dfrac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} + \left[\breve{S} - \breve{m}_1\left(\dfrac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\dfrac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right\}$
m_2	$-(m_1 + m_2)\left\{\left[\breve{V} + \breve{m}_2\left(\dfrac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\dfrac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} + \left[\breve{S} + \breve{m}_2\left(\dfrac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\dfrac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right\}$
U	$-(m_1 + m_2)\left\{\left(\dfrac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\left[(\breve{U} - T\breve{S})\left(\dfrac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} - \breve{V}\left(\left(\dfrac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\dfrac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right)\right] + \left(\dfrac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\left[(\breve{U} + p\breve{V})\left(\dfrac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p} - \breve{S}\left(\left(\dfrac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\dfrac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right)\right]\right\}$

Table IV-15
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

x, y, z / w', w	T, U, S
P	$-\breve{S}\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)$ [illegible]
m_1	[illegible] $- T\breve{S}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p}\right.$ [illegible] $- \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right] p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\Bigg\}$
m_2	$-(m_1 + m_2)\Bigg\{\left[(\breve{U} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} - \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right] p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\Bigg\}$
V	$(m_1 + m_2)\Bigg\{\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} - \breve{V}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right)\right] + \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p} - \breve{S}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right)\right]\Bigg\}$

Table IV-16
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

x, y, z / w', w	p, m_1, m_2
T	1
V	$(m_1 + m_2)\left(\frac{\partial \breve{v}}{\partial T}\right)_{\breve{m}_1}$ [illegible]
U	$(m_1 + m_2)\left[\breve{c}_p - p\left(\frac{\partial}{\partial}\right.\right.$ [illegible] $\left.\right]$
S	$(m_1 + m_2)\frac{\breve{c}_p}{T}$

Table IV-17
Jacobians of extensive functions for a
binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)} * \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

w' \ x, y, z	p. an V
T	$\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}$
m_2	$+ m_2)\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}$
U	$+ p\breve{V}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right)\Big]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}$ $- \breve{c}_p\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\Big\}$
S	$(m_1 + m_2)\left\{\frac{\breve{c}_p}{T}\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\right.$ $\left. - \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\right\}$

Table IV-18
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w^*, x, y, z)}{\partial(T, p, m_1, m_2)} = \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

w \ x, y, z	$p, \breve{m}_1, U$
T	$\breve{U} - \breve{m}_1\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p}$
m_2	$-(m_1 + m_2)\left[\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\right]$
V	$(m_1 + m_2)\left\{\left[(\breve{U} + p\breve{V}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} - \breve{c}_p\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\right\}$
S	$(m_1 + m_2)\left\{\frac{\breve{c}_p}{T}\left[(\breve{U} - T\breve{S}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right)\right] + \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right] p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\right\}$

Table IV-19
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, \breve{m}_1, \breve{m}_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, \breve{m}_1, \breve{m}_2)}$$

x, y, z / w', w	p, $\breve{m}_1$, S
T	[illegible]
[illegible]	$-(m_1 + m_2)\frac{\breve{C}_p}{T}$
V	$-(m_1 + m_2)\left\{\frac{\breve{C}_p}{T}\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right] - \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\right\}$
U	$-(m_1 + m_2)\left\{\frac{\breve{C}_p}{T}\left[(\breve{U} - T\breve{S}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right] + \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\right\}$

Table IV-20
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w,\ x,\ y,\ z)}{\partial(T,\ p,\ m_1,\ m_2)}$$

w \ x, y, z	$p,\ m_2,\ V$
T	$-\breve{V} - \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\ p}$
m_1	$(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\ \breve{m}_1}$
U	[illegible] $+ p\breve{V}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,\ p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\ p}\right)\Big]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\ \breve{m}_1}$ [illegible] $\breve{c}_p\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\ p}\right]\Big\}$
S	$-(m_1 + m_2)\left\{\frac{\breve{c}_p}{T}\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\ p}\right] - \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\ p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\ \breve{m}_1}\right\}$

Table IV-21
Jacobians of extensive functions for a binary systen of one phase

$$\frac{\partial(W', x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(W, x, y, z)}{\partial(T, p, m_1, m_2)}$$

x, y, z / W', W	p, m_1, U
T	$-\breve{U} - \breve{m}_2\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p}$
m_1	$(m_1 + m_2)\left[\breve{c}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\right]$
V	$-(m_1 + m_2)\left\{\left[(\breve{U} + p\breve{V}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} - \breve{c}_p\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\right\}$
•	$-(m_1 + m_2)\left\{-\frac{\breve{c}_p}{T}\left[(\breve{U} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right)\right]$ + [[illegible] $]_{p, \breve{m}_1}\}$

Table IV-22
Jacobians of extensive functions for a binary system of one phase

$$-\frac{\partial(T, x, y, z)}{\partial(T, p, m_1, m_2)}, \qquad \frac{\partial(T, x, y, z)}{\partial(T, p, m_1, m_2)}$$

w \ x, y, z	$p \ldots S$
T	$-\breve{S} - \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}$
m_1	$(m_1 + m_2)\frac{\breve{C}_p}{T}$
V	$(m_1 + m_2)\left\{\frac{\breve{C}_p}{T}\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right] - \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\right\}$
U	$(m_1 + m_2)\left\{\frac{\breve{C}_p}{T}\left[(\breve{U} - T\breve{S}) + \breve{m}_2\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p}\right] + \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right] p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\right\}$

Table IV-23
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)} \qquad \frac{\partial(w, x, y, z)}{\partial(T, p, \breve{m}_1, \breve{m}_2)}$$

x, y, z / w	$p, \breve{V}, \breve{U}$
T	W l / r ,P KdaJ T, p
m_1	$-(m_1 + m_2)\left\{\left[(\breve{U} + p\breve{V}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1} - \breve{c}_p\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right]\right\}$
m_2	$(m_1 + m_2)\left\{\left[(\breve{U} + p\breve{V}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1} - \breve{c}_p\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right]\right\}$
S	$(m_1 + m_2)\left\{\frac{\breve{c}_p}{T}\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - \breve{V}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right] - \left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p} - \breve{S}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\right\}$

Table IV-24
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

w', w \ x, y, z	p, V, S
T	$\breve{S}\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - \breve{V}\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}$
m_1	$(m_1 + m_2)\left\{\frac{\breve{c}_p}{T}\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right] - \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\right\}$
m_2	$-(m_1 + m_2)\left\{\frac{\breve{c}_p}{T}\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right] - \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\right\}$
U	$-(m_1 + m_2)\left\{\frac{\breve{c}_p}{T}\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - \breve{V}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right] - \left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p} - \breve{S}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\right\}$

Table IV-25
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

x, y, z / w', w	p, U, S
T	$\tilde{S}\left(\frac{\partial \tilde{U}}{\partial \tilde{m}_1}\right)_{T,p} - \tilde{U}\left(\frac{\partial \tilde{S}}{\partial \tilde{m}_1}\right)_{T,p}$
m_1	$(m_1 + m_2)\left\{\frac{\tilde{C}_p}{T}\left[(\tilde{U} - T\tilde{S}) - \tilde{m}_1\left(\left(\frac{\partial \tilde{U}}{\partial \tilde{m}_1}\right)_{T,p} - T\left(\frac{\partial \tilde{S}}{\partial \tilde{m}_1}\right)_{T,p}\right)\right]\right.$ $\left. + \left[\tilde{S} - \tilde{m}_1\left(\frac{\partial \tilde{S}}{\partial \tilde{m}_1}\right)_{T,p}\right] p\left(\frac{\partial \tilde{V}}{\partial T}\right)_{p,\tilde{m}_1}\right\}$
m_2	$(m_1 + m_2)\left\{\frac{\tilde{C}_p}{T}\left[(\tilde{U} - T\tilde{S}) + \tilde{m}_2\left(\left(\frac{\partial \tilde{U}}{\partial \tilde{m}_1}\right)_{T,p} - T\left(\frac{\partial \tilde{S}}{\partial \tilde{m}_1}\right)_{T,p}\right)\right]\right.$ $\left. + \left[\tilde{S} + \tilde{m}_2\left(\frac{\partial \tilde{S}}{\partial \tilde{m}_1}\right)_{T,p}\right] p\left(\frac{\partial \tilde{V}}{\partial T}\right)_{p,\tilde{m}_1}\right\}$
V	$(m_1 + m_2)\left\{\frac{\tilde{C}_p}{T}\left[(\tilde{U} - T\tilde{S})\left(\frac{\partial \tilde{V}}{\partial \tilde{m}_1}\right)_{T,p} - \tilde{V}\left(\left(\frac{\partial \tilde{U}}{\partial \tilde{m}_1}\right)_{T,p} - T\left(\frac{\partial \tilde{S}}{\partial \tilde{m}_1}\right)_{T,p}\right)\right]\right.$ $\left. - \left(\frac{\partial \tilde{V}}{\partial T}\right)_{p,\tilde{m}_1}\left[(\tilde{U} + p\tilde{V})\left(\frac{\partial \tilde{S}}{\partial \tilde{m}_1}\right)_{T,p} - \tilde{S}\left(\left(\frac{\partial \tilde{U}}{\partial \tilde{m}_1}\right)_{T,p} + p\left(\frac{\partial \tilde{V}}{\partial \tilde{m}_1}\right)_{T,p}\right)\right]\right\}$

Table IV-26
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

x, y, z / w', w	...... r
T	$(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}$
P	$-(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}$
U	$(m_1 + m_2)^2\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} + \breve{c}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right]$
S	$(m_1 + m_2)^2\left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right]$

Table IV-27
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}$$

w' \ x, y, z	m_1, m_2, U
T	$-(m_1 + m_2)\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} + p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right]$
p	$-(m_1 + m_2)\left[\breve{C}_p - p\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\right]$
V	$-(m_1 + m_2)^2\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} + \breve{C}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right]$
S	$-(m_1 + m_2)^2\left[p\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} + \frac{p\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right]$

Table IV-28
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, \breve{m}_1, \breve{m}_2)} = \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

w' \ x, y, z	m_1, m_2, S
T	$-(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}$
p	$-(m_1 + m_2)\frac{\breve{C}_p}{T}$
V	$-(m_1 + m_2)^2\left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} + \frac{\breve{C}_p}{T}$ [illegible]
U	$(m_1 + m_2)^2\left[p\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} + \frac{p\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right]$

Table IV-29
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)} \cdot \frac{\partial(w, x, y, z)}{\partial(T, p, \breve{m}_1, m_2)}$$

x, y, z / w	m_1, V, U
T	$-(m_1 + m_2)\left\{\left[(\breve{U} + p\breve{V}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1} + \left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right] T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\right\}$
P	$(m_1 + m_2)\left\{\left[(\breve{U} + p\breve{V}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right.\right.\right.$ [illegible] $- \breve{c}_p\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right]\right\}$
m_2	$(m_1 + m_2)^2\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} + \breve{c}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right]$
S	[illegible]

Table IV-30
Jacobians of extensive functions for a
binary system of one phase

$$\frac{\partial(w,\,x,\,y,\,z)}{\partial(T,\,p,\,m_1,\,m_2)}\,,\quad \frac{\partial(w,\,x,\,y,\,z)}{\partial(T,\,p,\,m_1,\,m_2)}$$

	m_1, V, S
T	$-(m_1+m_2)\left\{\left[\breve{V}-\breve{m}_1\left(\frac{\partial\breve{V}}{\partial\breve{m}_1}\right)_{T,\,p}\right]\left(\frac{\partial\breve{V}}{\partial T}\right)_{p,\,\breve{m}_1} + \left[\breve{S}-\breve{m}_1\left(\frac{\partial\breve{S}}{\partial\breve{m}_1}\right)_{T,\,p}\right]\left(\frac{\partial\breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right\}$
p	$-(m_1+m_2)\left\{\frac{\breve{c}_p}{T}\left[\breve{V}-\breve{m}_1\left(\frac{\partial\breve{V}}{\partial\breve{m}_1}\right)_{T,\,p}\right] - \left[\breve{S}-\breve{m}_1\left(\frac{\partial\breve{S}}{\partial\breve{m}_1}\right)_{T,\,p}\right]\left(\frac{\partial\breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}\right\}$
m_2	$(m_1+m_2)^2\left[\left(\frac{\partial\breve{V}}{\partial T}\right)^2_{p,\,\breve{m}_1} + \frac{\breve{c}_p}{T}\left(\frac{\partial\breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right]$
U	$(m_1+m_2)^2\left\{\left[(\breve{U}+p\breve{V}-T\breve{S}) - \breve{m}_1\left(\left(\frac{\partial\breve{U}}{\partial\breve{m}_1}\right)_{T,\,p} + p\left(\frac{\partial\breve{V}}{\partial\breve{m}_1}\right)_{T,\,p} - T\left(\frac{\partial\breve{S}}{\partial\breve{m}_1}\right)_{T,\,p}\right)\right] \times \left[\left(\frac{\partial\breve{V}}{\partial T}\right)^2_{p,\,\breve{m}_1} + \frac{\breve{c}_p}{T}\left(\frac{\partial\breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right]\right\}$

Table IV-31
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

w' \ w ; x, y, z	m_1, U, S
T	$-(m_1+m_2)\left\{\left[(\breve U - T\breve S) - \breve m_1\left(\left(\frac{\partial \breve U}{\partial \breve m_1}\right)_{T,p} - T\left(\frac{\partial \breve S}{\partial \breve m_1}\right)_{T,p}\right)\right]\left(\frac{\partial \breve V}{\partial T}\right)_{p,\breve m_1} - \left[\breve S - \breve m_1\left(\frac{\partial \breve S}{\partial \breve m_1}\right)_{T,p}\right]p\left(\frac{\partial \breve V}{\partial T}\right)_{p,\breve m_1}\right\}$
P	$-(m_1+m_2)\left\{\frac{\breve c_p}{T}\left[(\breve U - T\breve S) - \breve m_1\left(\left(\frac{\partial \breve U}{\partial \breve m_1}\right)_{T,p} - T\left(\frac{\partial \breve S}{\partial \breve m_1}\right)_{T,p}\right)\right] + \left[\breve S - \breve m_1\left(\frac{\partial \breve S}{\partial \breve m_1}\right)_{T,p}\right]p\left(\frac{\partial \breve V}{\partial T}\right)_{p,\breve m_1}\right\}$
m_2	$-(m_1+m_2)^2\left[p\left(\frac{\partial \breve V}{\partial T}\right)^2_{p,\breve m_1} + \frac{p\breve c_p}{T}\left(\frac{\partial \breve V}{\partial p}\right)_{T,\breve m_1}\right]$
V	$-(m_1+m_2)^2\left\{\left[(\breve U + p\breve V - T\breve S) - \breve m_1\left(\left(\frac{\partial \breve U}{\partial \breve m_1}\right)_{T,p} + p\left(\frac{\partial \breve V}{\partial \breve m_1}\right)_{T,p} - T\left(\frac{\partial \breve S}{\partial \breve m_1}\right)_{T,p}\right)\right]$ [illegible] $\right\}$

Table IV-32
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

w', w \ x, y, z	m_2, V, U
T	$(m_1 + m_2)\left\{\left[(\breve{U} + p\breve{V}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1} + \left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right]T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\right\}$
P	[illegible]
m_1	$-(m_1 + m_2)^2\left[T\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} + \breve{c}_p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right]$
S	$(m_1 + m_2)^2\left\{\left[(\breve{U} + p\breve{V} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\right.$ [illegible]

Table IV-33
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w, x, y, z)}{\partial(T, p, \breve{m}_1, m_2)}, \quad \frac{\partial(w, x, y, z)}{\partial(T, p, m_1, m_2)}$$

w \ x, y, z	m_2, V, S
T	$(m_1 + m_2)\left\{\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1} + \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right\}$
p	$(m_1 + m_2)\left\{\frac{\breve{C}_p}{T}\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}\right] - \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}\right\}$
m_1	$-(m_1 +$ [illegible] $\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}$
G	$-(m_1 + m_2)^2\left\{\left[(\breve{U} + p\breve{V} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} + \frac{\breve{C}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right]\right\}$

Table IV-34
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(W, x, y, z)}{\partial(T, p, m_1, m_2)} = \frac{\partial(W, x, y, z)}{\partial(T, p, \breve{m}_1, \breve{m}_2)}$$

W \ x, y, z	m_2, U, S
T	$(m_1 + m_2)\left\{\left[(\breve{U} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1} - \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]p\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right\}$
p	$(m_1 + m_2)\left\{\frac{\breve{c}_p}{T}\left[(\breve{U}$ [illegible] $) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p}\right.\right.\right.$ [illegible] $\left.\left.\left. - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right] + \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right]p\left(\frac{\partial \breve{V}}{\partial T}\right)_{T,\breve{m}_1}\right\}$
m_1	[illegible]
V	$(m_1 + m_2)^2\left\{\left[(\breve{U} + p\breve{V} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right] \cdot \left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p,\breve{m}_1} + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}\right]\right\}$

Table IV-35
Jacobians of extensive functions for a binary system of one phase

$$\frac{\partial(w', x, y, z)}{\partial(T, p, m_1, m_2)}, \quad \frac{\partial(V, x, y, z)}{\partial(T, p, m_1, m_2)}$$

x, y, z / w'	V, U, S
T	$-(m_1 + m_2)\left\{\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} - \breve{V}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right)\right] + \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p} - \breve{S}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right)\right]\right\}$
P	$-(m_1 + m_2)\left\{\frac{\breve{c}_p}{T}\left[(\breve{U} - T\breve{S})\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} - \breve{V}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right)\right] - \left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\left[(\breve{U} + p\breve{V})\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p} - \breve{S}\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right)\right]\right\}$
. .	$(m_1 + m_2)^2\left\{\left[(\breve{U} + p\breve{V} - T\breve{S}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right] \cdot \left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right]\right\}$
m_2	$-(m_1 + m_2)^2\left\{\left[(\breve{U} + p\breve{V} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T, p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right] \cdot \left[\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1} + \frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right]\right\}$

In order to obtain the first partial derivâtive of any one of the seven quantities, T, p, m_1, m_2, V, U, S with respect to any second quantity of the seven when any third, fourth, and fifth quantities of the seven are held constant, one has only to divide the value of the Jacobian in which the first letter in the first line is the quantity being differentiated and in which the second, third, and fourth letters in the first line are the quantities held constant by the value of the Jacobian in which the first letter of the first line is the quantity with respect to which the differentiation is taking place and in which the second, third, and fourth letters in the first line are the quantities held constant.

To obtain the relation among any seven derivatives having expressed them in terms of the same six derivatives,

$$\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\breve{m}_1}, \quad \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\breve{m}_1}, \quad \left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p}, \quad \breve{c}_p, \quad \left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p}, \quad \left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p},$$

one can then eliminate the six derivatives from the seven equations, leaving a single equation connecting the seven derivatives. In addition to the relations among seven derivatives there are also degenerate cases in which there are relations among fewer than seven derivatives.

In case a relation is needed that involves one or more of the thermodynamic potential functions $H = U + pV$, $A = U - TS$, $G = U + pV - TS$, partial derivatives involving one or more of these functions can also be calculated as the quotients of two Jacobians, which can themselves be calculated by the same method used to calculate the Jacobians in Tables IV-1 to IV-35.

It will be noted that the expressions for the Jacobians in Tables IV-1 to IV-35 are not symmetrical with respect to the two mass fractions $\breve{m}_1$ and $\breve{m}_2$. If the Jacobians in these Tables had been expressed in terms of the derivatives $\frac{\partial \breve{V}}{\partial \breve{m}_1}$, $\frac{\partial \breve{V}}{\partial \breve{m}_2}$, $\frac{\partial \breve{U}}{\partial \breve{m}_1}$, $\frac{\partial \breve{U}}{\partial \breve{m}_2}$, $\frac{\partial \breve{S}}{\partial \breve{m}_1}$, and $\frac{\partial \breve{S}}{\partial \breve{m}_2}$, with respect to the two mass fractions, $\breve{m}_1$ and $\breve{m}_2$, rather than in terms of the derivatives, $\frac{\partial \breve{V}}{\partial \breve{m}_1}$, $\frac{\partial \breve{U}}{\partial \breve{m}_1}$, and $\frac{\partial \breve{S}}{\partial \breve{m}_1}$, with respect to the single mass fraction, $\breve{m}_1$, the symmetry of the expressions for the Jacobians with respect to $\breve{m}_1$ and $\breve{m}_2$ would have been preserved, but the Jacobians would not have been expressed in terms of the minimum number of first derivatives. In this case it would not have been possible to use the expressions for the Jacobians directly to obtain a desired relation among any seven first derivatives of the quantities, T, p, $\breve{m}_1$, $\breve{m}_2$, $\breve{V}$, $\breve{U}$, and $\breve{S}$, by elimination of the first derivatives, $\frac{\partial \breve{V}}{\partial T}$, $\frac{\partial \breve{V}}{\partial p}$, $\frac{\partial \breve{V}}{\partial \breve{m}_1}$, $\frac{\partial \breve{V}}{\partial \breve{m}_2}$, $\breve{c}_p$, $\frac{\partial \breve{W}}{\partial \breve{m}_1}$, $\frac{\partial \breve{U}}{\partial \breve{m}_2}$, $\frac{\partial \breve{S}}{\partial \breve{m}_1}$, and $\frac{\partial \breve{S}}{\partial \breve{m}_2}$, from the seven equations for the seven first derivatives. Actually with the use of the Jacobians in Tables IV-1 to IV-35 which are expressed in terms of the minimum number of fundamental derivatives, $\frac{\partial \breve{V}}{\partial T}$, $\frac{\partial \breve{V}}{\partial p}$, $\frac{\partial \breve{V}}{\partial \breve{m}_1}$, $\breve{c}_p$, $\frac{\partial \breve{U}}{\partial \breve{m}_1}$, and $\frac{\partial \breve{S}}{\partial \breve{m}_1}$, in spite of the fact that these expressions are unsymmetrical with respect to $\breve{m}_1$ and $\breve{m}_2$, it does not make any difference in the final result which component is chosen as component 1 and which component is chosen as component 2. For example, if one thinks of a solution of water and ethyl alcohol and if water is chosen as component 1, then from Table IV-32 one obtains the derivative $\left(\frac{\partial S}{\partial \breve{m}_1}\right)_{m_2, V, U}$ equal to

$$-\frac{1}{T}\left[(\breve{U} + p\breve{V} - T\breve{S}) + \breve{m}_2\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right].$$

Now from Table IV-29 one obtains the derivative $\left(\frac{\partial S}{\partial m_2}\right)_{m_1, V, U}$ equal to

$$-\frac{1}{T}\left[(\breve{U} + p\breve{V} - T\breve{S}) - \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right].$$

On account of the fact that $\breve{m}_1 + \breve{m}_2 = 1$, one has $\left(\frac{\partial \breve{U}}{\partial \breve{m}_1}\right)_{T,p} = -\left(\frac{\partial \breve{U}}{\partial \breve{m}_2}\right)_{T,p}$. Thus $\left(\frac{\partial S}{\partial m_2}\right)_{m_1, V, U}$ is also equal to

$$-\frac{1}{T}\left[(\breve{U} + p\breve{V} - T\breve{S}) + \breve{m}_1\left(\left(\frac{\partial \breve{U}}{\partial \breve{m}_2}\right)_{T,p} + p\left(\frac{\partial \breve{V}}{\partial \breve{m}_2}\right)_{T,p} - T\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,p}\right)\right].$$

Consequently the same value would be obtained for the partial derivative of the total entropy with respect to the mass of water regardless of whether water were chosen as component 1 or as component 2.

Appendix A to Part IV

Equations for energy and entropy in the case of a binary system of one phase and of variable total mass developed on the basis of an expression for heat in the case of an open system

In the author's Carnegie Institution of Washington Publication No, 408A[1] equations were developed for energy and entropy in the case of open systems on the basis of an expression for the heat received by an open system. In the case of a binary system of one phase undergoing reversible changes of temperature, pressure, mass of component 1, and mass of component 2, the heat received was shown to be represented by the integral in the following equation

$$Q = \int_{T_0,\, p_0,\, m_{1_0},\, m_{2_0}}^{T,\, p,\, m_1,\, m_2} \left\{ \left(\frac{dQ}{dT}\right)_{p,\, m_1,\, m_2} dT + \left(\frac{dQ}{dp}\right)_{T,\, m_1,\, m_2} dp + \left(\frac{dQ}{dm_1}\right)_{T,\, p,\, m_2} dm_1 + \left(\frac{dQ}{dm_2}\right)_{T,\, p,\, m_1} dm_2 \right\}$$

$$= \int_{T_0,\, p_0,\, m_{1_0},\, m_{2_0}}^{T,\, p,\, m_1,\, m_2} \left\{ (m_1 + m_2)\, c_p dT + (m_1 + m_2)\, l_p dp + l_{m_1} dm_1 + l_{m_2} dm_2 \right\}, \qquad \text{(IV-A-1)}$$

where l_{m_1} denotes the reversible heat of addition of component 1 at constant temperature, constant pressure, and constant mass of component 2, and l_{m_2} denotes the reversible

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[1] Tunell, G., *Thermodynamic Relations in Open Systems*, Carnegie Institution of Washington Publication No. 408A, 1977.

heat of addition of component 2 at constant temperature, constant pressure, and constant mass of component 1.[2] In the case of a binary system of one phase undergoing reversible changes of temperature, pressure, mass of component 1, and mass of component 2, the energy change was shown to be represented by the integral in the following equation

$$U(T, p, m_1, m_2) - U(T_0, p_0, m_{1_0}, m_{2_0})$$

$$= \int_{T_0, p_0, m_{1_0}, m_{2_0}}^{T, p, m_1, m_2} \Bigg\{ (m_1 + m_2)\left[\breve{c}_p - p\frac{\partial \breve{V}}{\partial T}\right] dT + (m_1 + m_2)\left[\breve{l}_p - p\frac{\partial \breve{V}}{\partial p}\right] dp$$

$$+ \left[l_{m_1} - p\breve{m}_2\frac{\partial \breve{V}}{\partial \breve{m}_1} - p\breve{V} + \breve{H}'\right] dm_1$$

$$+ \left[l_{m_2} + p\breve{m}_1\frac{\partial \breve{V}}{\partial \breve{m}_1} - p\breve{V} + \breve{H}''\right] dm_2 \Bigg\}, \qquad \text{(IV-A-2)}$$

where $\breve{m}_1$ denotes the mass fraction of component 1, $\breve{m}_2$ denotes the mass fraction of component 2, $\breve{H}'$ denotes the specific enthalpy of pure component 1 in equilibrium with the binary solution across a semipermeable membrane permeable only to component 1, and $\breve{H}''$ denotes the specific enthalpy of pure component 2 in equilibrium with the binary solution across a semipermeable membrane permeable only to component 2.[3] In the

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[2] Tunell, G., Carnegie Institution of Washington Publication No. 408A, 1977, p. 40, equation (B-6), p. 42, equations (B-10), and (B-11), p, 46, equation (B-19), and P. 47, equation (B-20).

[3] Tunell, G., Carnegie Institution of Washington Publication No. 408A, 1977, p. 52, equation (B-35).

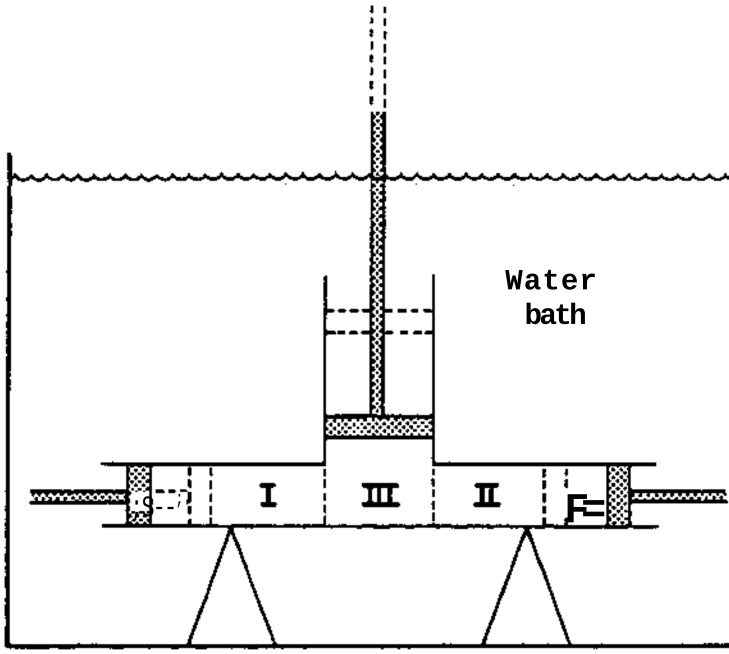

Figure IV-A-1

same case the entropy change was shown to be represented by the integral in the following equation

$$S(T, p, m_1, m_2) - S(T_0, p_0, m_{1_0}, m_{2_0})$$

$$= \int_{T_0, p_0, m_{1_0}, m_{2_0}}^{T, p, m_1, m_2} \left\{ (m_1 + m_2) \frac{\breve{c}_p}{T} dT + (m_1 + m_2) \frac{\breve{l}_p}{T} dp + \left[\frac{\breve{l}_{m_1}}{T} + \breve{S}' \right] dm_1 + \left[\frac{\breve{l}_{m_2}}{T} + \breve{S}'' \right] dm_2 \right\} ,$$

(IV-A-3)

where $\breve{S}'$ denotes the specific entropy of pure component 1 in equilibrium with the binary solution across a semipermeable membrane permeable only to component 1, and $\breve{S}''$ denotes the specific entropy of pure component 2 in equilibrium with the binary solution across a semipermeable membrane permeable only to component 2.[4,5] The derivation of these equations for heat, energy, and entropy was based on a detailed operational analysis of a system of three chambers immersed in a water bath the temperature of which could be controlled (Figure IV-A-1). Chambers I and II containing pure components 1 and 2 were separated by semipermeable membranes from chamber III, which contained a solution of components 1 and 2. The

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[4] **Tunell, G.,** Carnegie Institution of Washington **Publication** No. 408A, 1977, p. 56, equation (B-46).

[5] For an explanation of methods for obtaining experimental values for the l_B's see G. **Tunell,** Idem, pages 46 and 59-62.

membrane separating chambers I and III was supposed permeable only to component 1; similarly, the membrane separating chambers II and III was supposed permeable only to component 2. When the pressures exerted by the three pistons on the contents of the three chambers were changed with maintenance of osmotic equilibrium, causing movement of the three pistons, and when the temperature of the water bath was changed, causing a flow of heat to or from the materials in the three chambers, the change of energy of the materials in the three chambers, which together constituted a closed system, was given by the equation

$$U_2 - U_1 = Q - W, \qquad \text{(IV-A-4)}$$

where U_2 denotes the energy of the materials in the three chambers in the final state, U_1 denotes the energy of the materials in the three chambers in the initial state, Q denotes the heat received by the materials in the three chambers from the water bath (a positive or negative quantity), and W denotes the work done on the three pistons by the materials in the three chambers (a positive or negative quantity). Note that maintenance of osmotic equilibrium required that of the three pressures in the three chambers only one was independent, the other two were functions of the temperature, the concentration in chamber III, and the one pressure taken as independent. The materials in the three chambers I, II, and III, together constituted a closed system undergoing a reversible change of state. Consequently we have

$$S_2 - S_1 = \int_1^2 \frac{dQ}{T} , \qquad \text{(IV-A-5)}$$

where *Si* denotes the entropy of the materials in the three chambers in the final state and *S* denotes the entropy of the materials in the three chambers in the initial state. Thus the total change in energy and the total change in entropy of the closed system consisting of the materials in the three chambers were experimentally determinable. Finally, by subtraction of the energy changes of the pure components 1 and 2 in the side chambers I and II from the total energy change of the materials in the three chambers, the change in energy of the binary solution in chamber III as represented in equation (IV-A-2) was derived. Likewise by subtraction of the entropy changes of the pure components 1 and 2 in the side chambers I and II from the total entropy change of the materials in the three chambers, the change in entropy of the binary solution in chamber III as represented in equation (IV-A-3) was derived. For the details of these proofs the reader is referred to Appendix B of the author's Carnegie Institution of Washington Publication No. 408A.[6] It is to be noted that the only physical information used in the derivations of equations (IV-A-1), (IV-A-2), and (IV-A-3) in addition to the well established thermodynamic relations for closed systems, was the fact that when mass of constant composition is added reversibly to an open system of the same composition at constant temperature and constant pressure no heat is added.[7]

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[6] Tunell, G., Carnegie Institution of Washington Publication No. 408A, 1977, pp. 34-58.

[7] Cf. L.J. Gillesple and J.R. Coe, Jr., Jour. Phys. Chem., Vol. 1, p. 105, 1933, and G. Tunell, Carnegie Institution of Washington Publication No. 408A, 1977, pp. 18-24.

It was not necessary to make use of any definition of work in the case of an open system when masses are being transferred to or from the system in the derivation of equations (IV-A-1), (IV-A-2), and (IV-A-3). However, according to the definition of work done by an open system used by Goranson[8] and by Van Wylen[9] we have

$$dW = pdV \,. \qquad \text{(IV-A-6)}$$

In Appendix A to Part II of this text reasons for the acceptance of this definition of work in the case of an open system when masses are being transferred to or from the system were set forth in detail.

The correct differential equation for the energy change in an open system, when use is made of definitions of heat received and work done in the case of open systems, was given by Hall and Ibele in their treatise entitled *Engineering Thermodynamics.* They[10] stated that "A general equation for energy change in an open system can be written

$$dE = dQ - dW + \sum_i (e + pv)_i dm_i . \qquad (7.25)"$$

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[8] Goranson, R.W., Carnegie Institution of Washington Publication No. 408, 1930, pp. 39, 44.

[9] Van Wylen, G.J., *Thermodynamics,* John Wiley and Sons Inc., New York, 1959, pp. 49, 75-77, 80.

[10] Hall, N.A., and W.E., Ibele, *Engineering Thermodynamics*, Prentice-Hall, Inc., Englewood Cliffs, N.J., 1960, p. 108.

In this equation *dE* denotes the energy change of the open system, *dQ* the heat received by the open system, *dW* the work done by the open system, e the specific energy of pure component i in equilibrium with the open system across a semipermeable membrane permeable only to component i, p the pressure of pure component i in equilibrium with the open system across a membrane permeable only to component i, and *v* the specific volume of pure component i in equilibrium with the open system across a semipermeable membrane permeable only to component *i*. This equation is consistent with equation (IV-A-2) of this text as well as with the equation of Gillespie and Coe and with the Gibbs differential equation, as we proceed to show. According to Gillespie and Coe[11]

$$dS = \frac{dQ}{T} + \sum_i \breve{S}_i dm_i ,$$

where *dS* denotes the increase in entropy of an open system, *dQ* the heat received by the open system, $\breve{S}_j$ the specific entropy of pure component i in equilibrium with the open system across a semipermeable membrane permeable only to component i, and *dwj* the mass of component i added to the open system. Thus we have

$$dQ = TdS - \sum_i T\breve{S}_i dm_i .$$

Substituting this value of *dQ* in the equation of Hall and

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[11] Gillespie, L.J., and J.R.. Coe, Jr., Jour. Chenu Phys., 1, 105, 1933.

Ibele we have

$$dU = TdS - dW + \sum_i (\breve{U}_i + p\breve{V}_i - T\breve{S}_i) dm_i .$$

According to Goranson,[12] Van Wylen,[13] and Professor Wild[14]

$$dW = pdV$$

in the case of an open system. Thus we obtain

$$dU = TdS - pdV + \sum_i \breve{G}_i dm_i ,$$

where $\breve{G}_i$ denotes the specific Gibbs function of pure component i in equilibrium with the solution across a semipermeable membrane permeable only to component i. Since Gibbs proved that at equilibrium the chemical potentials of a component on both sides of a semipermeable membrane are equal and since the chemical potential u of a pure component is equal to the specific Gibbs function of this component, we thus arrive at the result

$$dU = TdS - pdV + \sum_i \mu_i dm_i ,$$

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[12] Goranson, R. ., Carnegie Institution of Washington Publication No, 408, 1930, pp. 39 and 44.

[13] Van Wylen, op. cit, pp. 49, 75-77, 80.

[14] Private communication from Professor R.L. Wild, who was formerly the Chairman of the Physics Department of the University of California at Riverside.

where y^ denotes the chemical potential of component *i* in the open system (solution) and *dm*± denotes the mass of component i added to the open system. We have thus demonstrated that the equation of Gillespie and Coe and the equation of Hall and Ibele are consistent with the Gibbs differential equation.

Appendix B to Part IV

Transformation of the work and heat line integrals from one coordinate space to other coordinate spaces in the case of a binary system of one phase and of variable total mass

As in the case of a one component system of one phase and of variable mass it is also true in the case of a binary system of one phase and of variable total mass that it is not necessary to define either work or heat when masses are being transferred to or from the system in order to obtain the energy and the entropy as functions of the absolute thermodynamic temperature, the pressure, and the masses of the two components from experimental measurements. Thus the derivation of the Jacobians listed in Tables IV-1 to IV-35 did not depend upon definitions of work done or heat received in the case of a binary system of one phase and of variable total mass when masses are being transferred to or from the system.

For some purposes, however, it is useful to have definitions of work and heat in the case of a binary system of one phase and of variable total mass. If the conclusion of Van Wylen and Professor Wild be accepted that it cannot be said that work is done at a stationary boundary across which mass is transported, then the work W done by a binary system of one phase and of variable total mass can be represented by the line integral

$$W = \int_{T_0,\, p_0,\, m_{1_0},\, m_{2_0}}^{T_f,\, p_f,\, fill\$\ 21?2} \left\{ p\, f dT + p \wedge dp + p f_{idmi} + p f \pounds <* \, n_2 \right\} \qquad \text{(IV-B-1)}$$

in (T, p, m_1, m_2)-space. Furthermore it was shown in Appendix IV-A that the heat 0 received by such a system is represented by the line integral

$$\int_{T_0, p_0, m_{1_0}, m_{2_0}}^{T, p, m_1, m_2} \ldots + m_2)\bar{l}_p dp + l_{m_1} dm_1 + l_{m_2} dm_2 \Big\} \qquad \text{(IV-B-2)}$$

in (T, p, m_1, m_2)-space, where l_{m_1} denotes the reversible heat of addition of component 1 at constant temperature, constant pressure and constant mass of component 2, and l_{m_2} denotes the reversible heat of addition of component 2 at constant temperature, constant pressure, and constant mass of component 1. In order to obtain the total derivative of the work done along a straight line parallel to one of the coordinate axes in any other coordinate space one obtains from Tables IV-1 to IV-35 the partial derivative of the volume with respect to the quantity plotted along that axis when the quantities plotted along the other axes are held constant and one multiplies this partial derivative by the pressure. The total derivative of the heat received along a straight line parallel to one of the coordinate axes in any other space, on the other hand, cannot be obtained by multiplication of the partial derivative of the entropy by the absolute thermodynamic temperature when reversible transfers of masses to or from the system are involved. In such cases the total derivatives of the heat received along lines parallel to coordinate axes in any desired coordinate space can be derived in terms of the total derivatives of the heat received along lines parallel to the coordinate axes in (T, p, m_1, m_2)-space by transformation of the heat line integrals by an extension of the method set forth in Appendix C to Part II. Following is an example of such a transformation. In the case of a binary system of one phase and of variable total mass the heat line integral extended along a path in (T, m_1, m_2, V)-space is

$$Q = \int_{T_0, m_{1_0}, m_{2_0}, V_0}^{T, m_1, m_2, V} \left\{ \left(\frac{dQ}{dT}\right)_{m_1, m_2, V} dT + \left(\frac{dQ}{dm_1}\right)_{T, m_2, V} dm_1 + \left(\frac{dQ}{dm_2}\right)_{T, m_1, V} dm_2 + \left(\frac{dQ}{dV}\right)_{T, m_1, m_2} dV \right\}$$

$$= \int_{T_0, m_{1_0}, m_{2_0}, V_0}^{T, m_1, m_2, V} \left\{ (m_1 + m_2)\breve{c}_V dT + \left(\frac{dQ}{dm_1}\right)_{T, m_2, V} dm_1 + \left(\frac{dQ}{dm_2}\right)_{T, m_1, V} dm_2 + l_V dV \right\} . \tag{IV-B-3}$$

The derivatives $\left(\frac{dQ}{dT}\right)_{m_1, m_2, V}$, $\left(\frac{dQ}{dm_1}\right)_{T, m_2, V}$, $\left(\frac{dQ}{dm_2}\right)_{T, m_1, V}$, and $\left(\frac{dQ}{dV}\right)_{T, m_1, m_2}$ can then be evaluated as quotients of two determinants. Thus we have

$$\left(\frac{\partial Q}{\partial T}\right)_{m_1, m_2, V} = (m_1 + m_2)\breve{c}_v = \frac{\begin{vmatrix} \frac{\partial Q}{\partial T} & \frac{\partial Q}{\partial p} & \frac{\partial Q}{\partial m_1} & \frac{\partial Q}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}}{\begin{vmatrix} \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}}$$

$$= \left\{ \frac{\partial Q}{\partial T}\left[\frac{\partial V}{\partial p}\right] - \frac{\partial Q}{\partial p}\left[\frac{\partial V}{\partial T}\right] + \frac{\partial Q}{\partial m_1}\left[\;\right] - \frac{\partial Q}{\partial m_2}\left[\;\right] \right\}$$

$$\div \left\{ 1 \cdot \left[\frac{\partial V}{\partial p}\right] - 0 \cdot \left[\frac{\partial V}{\partial T}\right] + 0 \cdot \left[0\right] - 0 \cdot \left[0\right] \right\}$$

$$= \left\{ (m_1 + m_2)^2 \breve{c}_p \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1} - (m_1 + m_2)^2 \breve{l}_p \left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1} \right\}$$

$$\div \left\{ (m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1} \right\}$$

$$= \left\{ (m_1 + m_2)\left[\breve{c}_p \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1} + T\left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1}\right]\right\} \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}, \tag{IV-B-4}$$

$$\left(\frac{\partial Q}{\partial m_1}\right)_{T,\,m_2,\,V} = \frac{\begin{vmatrix} \frac{\partial Q}{\partial T} & \frac{\partial Q}{\partial p} & \frac{\partial Q}{\partial m_1} & \frac{\partial Q}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}}{\begin{vmatrix} \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}}$$

$$= \left\{ dT[\;] - dp\left[\;\partial m_1\;\right] + dm_1\left[\;\partial p\;\right] - dm_2[0] \right\}$$

$$\div \left\{ 0[0] - 0\left[-\frac{\partial V}{\partial m_1}\right] + \frac{\partial m_1}{\partial m_1}\left[-\frac{\partial V}{\partial p}\right] - 0[0] \right\}$$

$$= \left\{ (m_1 + m_2)\,\breve{l}_p \left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}\right] - l_{m_1}(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1} \right\}$$

$$\div \left\{ -(m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1} \right\}$$

$$= \left\{ T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}\right] + l_{m_1}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1} \right\} \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1},$$

(IV-B-5)

$$\left(\frac{\partial Q}{\partial m_2}\right)_{T,\,m_1,\,V} = \frac{\begin{vmatrix} \frac{\partial Q}{\partial T} & \frac{\partial Q}{\partial p} & \frac{\partial Q}{\partial m_1} & \frac{\partial Q}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}}{\begin{vmatrix} \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \end{vmatrix}}$$

$$= \left\{\frac{\partial Q}{\partial T}\left[0\right] - \frac{\partial Q}{\partial p}\left[\frac{\partial V}{\partial m_2}\right] + \frac{\partial Q}{\partial m_1}\left[0\right] - \frac{\partial Q}{\partial m_2}\left[-\frac{\partial V}{\partial p}\right]\right\}$$

$$\div \left\{0\cdot\left[0\right] - 0\cdot\left[\frac{\partial V}{\partial m_2}\right] + 0\cdot\left[0\right] - \frac{\partial m_2}{\partial m_2}\left[-\frac{\partial V}{\partial p}\right]\right\}$$

$$= \left\{-(m_1+m_2)\breve{l}_p\left(\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}\right) + l_{m_2}(m_1+m_2)\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right\}$$

$$\div \left\{(m_1+m_2)\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right\}$$

$$= \left\{T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}\right] + l_{m_2}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right\} \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1},$$

(IV-B-6)

$$\left(\frac{\partial Q}{\partial V}\right)_{T,\, m_1,\, m_2} = l_V = \frac{\begin{vmatrix} \frac{\partial Q}{\partial T} & \frac{\partial Q}{\partial p} & \frac{\partial Q}{\partial m_1} & \frac{\partial Q}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \end{vmatrix}}{\begin{vmatrix} \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} & \frac{\partial V}{\partial m_1} & \frac{\partial V}{\partial m_2} \\ \frac{\partial T}{\partial T} & \frac{\partial T}{\partial p} & \frac{\partial T}{\partial m_1} & \frac{\partial T}{\partial m_2} \\ \frac{\partial m_1}{\partial T} & \frac{\partial m_1}{\partial p} & \frac{\partial m_1}{\partial m_1} & \frac{\partial m_1}{\partial m_2} \\ \frac{\partial m_2}{\partial T} & \frac{\partial m_2}{\partial p} & \frac{\partial m_2}{\partial m_1} & \frac{\partial m_2}{\partial m_2} \end{vmatrix}}$$

$$= \left\{ \frac{\partial Q}{\partial T}\begin{bmatrix}0\end{bmatrix} - \frac{\partial Q}{\partial p}\begin{bmatrix}1\end{bmatrix} + \frac{\partial Q}{\partial m_1}\begin{bmatrix}0\end{bmatrix} - \frac{\partial Q}{\partial m_2}\begin{bmatrix}0\end{bmatrix} \right\}$$

$$\div \left\{ \frac{\partial V}{\partial T}\begin{bmatrix}0\end{bmatrix} - \frac{\partial V}{\partial p}\begin{bmatrix}1\end{bmatrix} + \frac{\partial V}{\partial m_1}\begin{bmatrix}0\end{bmatrix} - \frac{\partial V}{\partial m_2}\begin{bmatrix}0\end{bmatrix} \right\}$$

$$= \left\{ (m_1 + m_2)\breve{l}_p \right\} \div \left\{ (m_1 + m_2)\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1} \right\}$$

$$= \left\{ -T\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\, \breve{m}_1} \right\} \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\, \breve{m}_1} .$$

(IV-B-7)

The corresponding values of the partial derivatives of the entropy obtained from Tables IV-26, IV-10, IV-7, and IV-6 are as follows:

$$\left(\frac{\partial S}{\partial T}\right)_{m_1, m_2, V} = \left\{(m_1 + m_2)\left[\frac{\breve{c}_p}{T}\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1} + \left(\frac{\partial \breve{V}}{\partial T}\right)^2_{p, \breve{m}_1}\right]\right\} \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1},$$

(IV-B-8)

$$\begin{aligned}\left(\frac{\partial S}{\partial m_1}\right)_{T, m_2, V} &= \left\{\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\right. \\ &\quad \left. + \left[\breve{S} + \breve{m}_2\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right\} \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1} \\ &= \left\{\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\right. \\ &\quad \left. + \left[\left(\frac{\partial S}{\partial m_1}\right)_{T, p, m_2}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right\} \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1} \\ &= \left\{\left(\frac{\partial \breve{V}}{\partial T}\right)_{p, \breve{m}_1}\left[\breve{V} + \breve{m}_2\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T, p}\right]\right. \\ &\quad \left. + \left[\frac{l_{m_1}}{T} + \breve{S}'\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1}\right\} \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T, \breve{m}_1},\end{aligned}$$

(IV-B-9)

$$\left(\frac{\partial S}{\partial m_2}\right)_{T,\,m_1,\,V} = \left\{\left[\breve{V} - \breve{m}_1\left(\frac{\partial \breve{V}}{\partial \breve{m}_1}\right)_{T,\,p}\right]\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}\right.$$

$$\left. + \left[\breve{S} - \breve{m}_1\left(\frac{\partial \breve{S}}{\partial \breve{m}_1}\right)_{T,\,p}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right\} \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}$$

$$= \left\{\left[\breve{V} - \breve{m}_1\left(\frac{\partial}{\partial} \text{[illegible]}\right.\right.\right.$$

$$\left. + \left[\left(\frac{\partial S}{\partial m_2}\right)_{T,\,p,\,m_1}\right]\left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}\right\} \div \left(\frac{\partial \breve{V}}{\partial p}\right)_{T,\,\breve{m}_1}$$

$$= \left\{\left(\frac{\partial \breve{V}}{\partial T}\right)_{p,\,\breve{m}_1}\left[\breve{V} - \text{[illegible]}\left(\frac{\partial \breve{V}}{\text{[illegible]}}\right)_{T,\,p}\right]\right.$$

$$\left. + \left[\frac{l_{m_2}}{T} + \breve{S}''\right]\left(\frac{\partial \breve{V}}{\text{[illegible]}}\right)_{\text{[illegible]}\,\breve{m}_1}\right\} \div \left(\frac{\text{[illegible]}}{\partial p}\right)_{T,\,\breve{m}_1}, \quad [1]$$

(IV-B-10)

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[1] From equations (IV-22) and (IV-23) we have

$\partial m_1)_{T,\,p,\,\text{[illegible]}}$ [illegible] $\partial \breve{m}_1)_{T,\,p}$ [illegible] $\partial m_2)_{T,\,p,\,\text{[illegible]}}$ [illegible] $\breve{m}_1\left(\overline{\partial \breve{m}_1}\right)_{T,\,p}$ [illegible].

Also from equation (XV-A-3) we have $\left(\frac{\partial \breve{S}}{\partial m_1}\right)_{T,\,p,\,m_2}$ = [illegible] + $\breve{S}'$

and $\left(\frac{\partial S}{\partial m_2}\right)_{T,\,p,\,m_1}$ = [illegible] + $\breve{S}''$, where $\breve{S}'$ denotes the specific entropy of pure component 1 in equilibrium with the binary solution across a semipermeable membrane permeable only to component 1, and $\breve{S}''$ the specific entropy of pure component 2 in equilibrium with the binary solution across a semipermeable membrane permeable only to component 2,

and

$$(as)_{T,\, m_1,\, m_2} \quad \_\,[\; \text{fiil})_{p,\, m_1} \quad \text{Lfll})_{T,\, m_1} \; . \qquad \text{(iv-B-ii)}$$

Thus it follows from (IV-B-4), (IV-B-7), (IV-B-8), and (IV-B-11) that

$$\left(\mathbf{f}\right)_{m_1,\, m_2,\, V} = T\left(\frac{\partial S}{\partial T}\right)_{m_1,\, m_2,\, V} \qquad \text{(IV-B-12)}$$

and

$$\left(\S\right) \quad , \quad T(\S) \qquad \text{(IV-B-U)}$$

but, finally, it also follows from (IV-B-5), (IV-B-6) (IV-B-9), and (IV-B-10) that

$$\left(\frac{dQ}{dm_1}\right)_{T,\, m_2,\, V} \neq T\left(\frac{\partial S}{\partial m_1}\right)_{T,\, m_2,\, V} \qquad \text{(IV-B-14)}$$

and

$$(f)_{T,\, m_1,\, V} \neq \text{jf!\^{}}\,)_{T,\, m_1,\, V} \; . \qquad \text{(IV-B-15)}$$

Appendix C to Part IV

Discussion of the tables of thermodynamic formulas for multi-component systems presented in Carnegie Institution of Washington Publication No. 408 by R.W. Goranson

On account of the fact that Goranson accepted the erroneous assumption of Sir Joseph Larmor[1] that in the case of the Gibbs differential equation,

$$dU = TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2 \ldots + \mu_n dm_n,$$

TdS represents dQ and that dQ represents an infinitesimal amount of heat which is acquired in a specified state of the system at a temperature T, Goranson's basic equations for the energy and the entropy of a multi-component system are incorrect. Goranson's equation for the energy change of a binary system undergoing changes of temperature, pressure, and masses of the two components

$$U(T, p, m_1, m_2) - U(T_0, p_0, m_{1_0}, m_{2_0})$$

$$= \int_{T_0,\, p_0,\, m_{1_0},\, m_{2_0}}^{T,\, p,\, m_1,\, m_2} \Big\{ (m_1 + m_2)\Big[c_p - p\Big(\frac{\partial \bar{v}}{\partial T}\Big)_p\Big] dT + (m_1 + m_2)\Big[l_p - p\Big(\frac{\partial \bar{v}}{\partial p}\Big)_T\Big] dp$$

$$+ \Big[l_{m_1} - p\bar{m}_2\frac{\partial \bar{v}}{\partial \bar{m}_1} - p\bar{v} + \mu_1\Big] dm_1 + \Big[l_{m_2} + p\bar{m}_1 \ldots - p\bar{v} + \mu_2\Big] dm_2 \Big\},[2] \quad \text{(IV-C-1)}$$

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[1] Larmor, Sir Joseph, Proc. Roy. Soc. London, 75, 289-290, 1905.

[2] Goranson, R.W., Carnegie Institution of Washington Publication No. 408, 1930, the first equation in §32 on page 48.

where l_{m_1} denotes the reversible heat of addition of component 1 at constant temperature, constant pressure, and constant mass of component 2, l_{m_2} denotes the reversible heat of addition of component 2 at constant temperature, constant pressure, and constant mass of component 1, $\breve{m}_1$ denotes the mass fraction $m_1/(m_1 + m_2)$, $\breve{m}_2$ denotes the mass fraction $m_2/(m_1 + m_2)$, μ_1 denotes the chemical potential of component 1, and μ_2 denotes the chemical potential of component 2, should be replaced by equation (IV-A-2) of this text which is repeated here as aquation (IV-C-2)

$$U(T, p, m_1, m_2) - U(T_0, p_0, m_{1_0}, m_{2_0})$$

$$= \int_{T_0, p_0, m_{1_0}, m_{2_0}}^{T, p, m_1, m_2} \Big\{ (m_1 + m_2)\Big[c_p - p\frac{\partial V}{\partial T}\Big]dT + (m_1 + m_2)\Big[l_p - p\frac{\partial V}{\partial p}\Big]dp$$

$$+ \Big[l_{m_1} - p\breve{m}_2\frac{\partial \breve{V}}{\partial \breve{m}_1} - p\breve{V} + \breve{H}'\Big]dm_1 + \Big[l_{m_2} + p\breve{m}_1\frac{\partial \breve{V}}{\partial \breve{m}_1} - p\breve{V} + \breve{H}''\Big]dm_2\Big\},$$

(IV-C-2)

where $\breve{H}'$ and $\breve{H}''$ denote the specific enthalpies of the pure components 1 and 2 in equilibrium with the solution across semipermeable membranes permeable only to components 1 and 2, respectively. Similar corrections are to be applied in the incorrect equation for the energy U in the case of a multi-component system on page 60 of Carnegie Institution of Washington Publication No. 408 [equation (1) in §41].

Likewise Goranson's equation for the entropy change of a binary system undergoing reversible changes of temperature, pressure, and masses of the two components, the first equation in §52 [equation (2)] on page 52 of Carnegie Institution of Washington Publication No. 408

$$S(T, p, m_1, m_2) - S(T_0, p_0, m_{1_0}, m_{2_0})$$

$$= \int_{T_0, p_0, m_{1_0}, m_{2_0}}^{T, p, m_1, m_2} \left\{ (m_1 + m_2)\frac{\breve{c}_p}{T} dT + (m_1 + m_2)\frac{\breve{l}_p}{T} dp \right.$$

$$\left. + \frac{l_{m_1}}{T} dm_1 + \frac{l_{m_2}}{T} dm_2 \right\} \qquad \text{(IV-C-3)}$$

should be replaced by equation (IV-A-3) of this text which is repeated here as equation (IV-C-4)

$$S(T, p, m_1, m_2) - S(T_0, p_0, m_{1_0}, m_{2_0})$$

$$= \int_{T_0, p_0, m_{1_0}, m_{2_0}}^{T, p, m_1, m_2} \left\{ (m_1 + m_2)\frac{\breve{c}_p}{T} dT + (m_1 + m_2)\frac{\breve{l}_p}{T} dp \right.$$

$$\left. + \left[\frac{l_{m_1}}{T} + \breve{s}'\right] dm_1 + \left[\frac{l_{m_2}}{T} + \breve{s}''\right] dm_2 \right\}, \qquad \text{(IV-C-4)}$$

where S' denotes the specific entropy of pure component 1 in equilibrium with the binary solution across a semipermeable membrane permeable only to component 1, and S'' denotes the specific entropy of pure component 2 in equilibrium with the binary solution across a semipermeable membrane permeable only to component 2. Similar corrections are to be applied to the incorrect equation for the entropy S in the case of a multi-component system on page 64 of Carnegie Institution of Washington Publication No. 408 (first equation in §43).

In Goranson's Tables of Thermodynamic Relations for First Derivatives expressions are listed such that any first derivative of one of the quantities, absolute thermodynamic temperature, pressure, mass of a component, volume, energy, entropy, Gibbs function, enthalpy, Helmholtz function, work, or heat with respect to any second of these quantities, certain other quantities being held constant, should be obtainable in terms of the standard derivatives,

$$\left(\frac{\partial v}{\partial p}\right)_{T, m_1, \ldots, m_n}, \quad \left(\frac{\partial v}{\partial T}\right)_{p, m_1, \ldots, m_n}, \quad \left(\frac{\partial v}{\partial m_k}\right)_{T, p, m_i}, \quad c_p, \quad m_i \text{ denoting}$$

all the component masses except m_k, $(m_1 + \ldots + m_n) c_p = C_p$, $i = 1, \ldots, n$, and μ_k, $k = 1, \ldots, n$, by division of one of the listed expressions by a second listed expression, the same quantities being held constant in each of these two listed expressions.

The expressions listed by Goranson for first derivatives in his Groups 1-8 are for the case in which all masses are held constant and are the same as the expressions listed by Bridgman for this case and the same as the Jacobians listed in Table 1-1 of this text. Unfortunately very many of the expressions listed by Goranson in his remaining Groups for first derivatives (Groups 9 - 162) are invalidated by his erroneous assumption that $dQ = TdS$ when there is reversible transfer of mass as well as heat. Thus for example in Goranson's Group 18 in which p, m_i, and S are held constant the following expressions are listed:

Group 18
(According to Goranson, Carnegie Institution of Washington Publication No. 408, p. 181)

p, m_i, S constant

$$(\partial T) = -\frac{l_{m_k}}{T}$$

$$(\partial m_k) = (m_1 + \ldots + m_n)\frac{\breve{c}_p}{T}$$

$$(\partial V) = -\frac{l_{m_k}}{T}\frac{\partial V}{\partial T} + \frac{\breve{c}_p(m_1 + \ldots + m_n)}{T}\frac{\partial V}{\partial m_k}$$

$$(\partial U) = \frac{p}{T}\, l_{m_k}\frac{\partial V}{\partial T} + (m_1 + \ldots + m_n)\frac{\breve{c}_p}{T}\left[\mu_k - p\frac{\partial V}{\partial m_k}\right]$$

$$(\partial G) = \frac{1}{T}\left[S l_{m_k} + (m_1 + \ldots + m_n)\breve{c}_p\mu_k\right]$$

$$(\partial H) = \frac{1}{T}(m_1 + \ldots + m_n)\breve{c}_p\mu_k$$

$$(\partial A) = \frac{1}{T}\left[l_{m_k}\left(S + p\frac{\partial V}{\partial T}\right) + (m_1 + \ldots + m_n)\breve{c}_p\left(\mu_k - p\frac{\partial V}{\partial m_k}\right)\right]$$

$$(dW) = p\frac{l_{m_k}}{T}\frac{\partial V}{\partial T} - \frac{\breve{c}_p(m_1 + \ldots + m_n)}{T}\, p\frac{\partial V}{\partial m_k}$$

$$(dQ) = 0$$

The corrected expressions for this group when account is taken of the equation of Gillespie and Coe are given in the following table

Group 18

(Corrected by G. Tunell)

p, m_j, S constant

$$\dot{k} = -\frac{l_{m_k}}{T} - \breve{S}_k$$

$$(\partial m_k) = (m_1 + \ldots + m_n)\frac{\breve{c}_p}{T}$$

$$(\partial V) = -\frac{\partial S}{\partial m_k}\frac{\partial V}{\partial T} + \frac{\breve{c}_p(m_1 + \ldots + m_n)}{T}\frac{\partial V}{\partial m_k}$$

$$= \left(-\frac{l_{m_k}}{T} - \breve{S}_k\right)\frac{\partial V}{\partial T} + \frac{\breve{c}_p(m_1 + \ldots + m_n)}{T}\frac{\partial V}{\partial m_k}$$

$$(\partial U) = p\frac{\partial S}{\partial m_k}\frac{\partial V}{\partial T} + (m_1 + \ldots + m_n)\frac{\breve{c}_p}{T}\left[\mu_k - p\frac{\partial V}{\partial m_k}\right]$$

$$= p\left(\frac{l_{m_k}}{T} + \breve{S}_k\right)\frac{\partial V}{\partial T} + (m_1 + \ldots + m_n)\frac{\breve{c}_p}{T}\left[\mu_k - p\frac{\partial V}{\partial m_k}\right]$$

$$(\partial G) = \left[S\frac{\partial S}{\partial m_k} + (m_1 + \ldots + m_n)\frac{\breve{c}_p\mu_k}{T}\right]$$

$$= \frac{1}{T}\left[S\left(l_{m_k} + T\breve{S}_k\right) + (m_1 + \ldots + m_n)\breve{c}_p\mu_k\right]$$

$$(\partial H) = \frac{1}{T}(m_1 + \ldots + m_n)\breve{c}_p\mu_k$$

$$(\partial A) = \frac{\partial S}{\partial m_k}\left(S + p\frac{\partial V}{\partial T}\right) + (m_1 + \ldots + m_n)\frac{\breve{c}_p}{T}\left(\mu_k - p\frac{\partial V}{\partial m_k}\right)$$

$$= \frac{1}{T}\left\{\left(l_{m_k} + T\breve{S}_k\right)\left(S + p\frac{\partial V}{\partial T}\right) + (m_1 + \ldots + m_n)\breve{c}_p\left[\mu_k - p\frac{\partial V}{\partial m_k}\right]\right\}$$

$$(\partial W) = p\left(\frac{l_{m_k}}{T} + \breve{S}_k\right)\frac{\partial V}{\partial T} - \frac{\breve{c}_p(m_1 + \ldots + m_n)}{T}p\frac{\partial V}{\partial m_k}$$

$$(\partial Q) = -(m_1 + \ldots + m_n)\breve{c}_p\breve{S}_k$$

In the corrected Table for Group 18, $\breve{S}^k$ denotes the specific entropy of pure component k in equilibrium with the multicomponent solution across a semipermeable membrane permeable only to component k.[3] In a good many cases Goranson's expressions involving the term l_{m_k} can be corrected by the substitution of $(l_{m_k} + \breve{S}^k)$ for l_{m_k}. However, in some cases this substitution does not make the necessary correction.

In conclusion it may be noted that the principal differences between Goranson's Tables and the present author's Tables are caused by Goranson's erroneous assumption that $\left(\frac{\partial S}{\partial m_k}\right)_{T,p,m_j} = \frac{l_{m_k}}{T}$, m_j denoting all the component masses except m_k, whereas in reality $\left(\frac{\partial S}{\partial m_k}\right)_{T,p,m_j} = \frac{l_{m_k}}{T} + \breve{S}^k$ and by Goranson's use of 3n + 3 standard derivatives, whereas in reality all the partial derivatives with respect to the various thermodynamic quantities can be expressed in terms of 3n fundamental derivatives, as Goranson himself recognized.[4]

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[3] It may be noted that the expressions in the table for Group 18 as corrected by the present author are consistent with the expressions in Table IV-22 of this text, although they differ in appearance from the expressions in Table IV-22.

[4] Goranson supplied an auxiliary table (Table A on page 149 of Carnegie Institution of Washington Publication 408) which is intended to permit the expression of the 3n + 3 standard derivatives in terms of 3n fundamental derivatives and the masses of the components. However, Goranson's Table A is also partly invalidated by his incorrect assumption that

$$\left(\frac{\partial S}{\partial m_k}\right)_{T,p,m_j} = \frac{l_{m_k}}{T}.$$