

THE DETERMINATION OF THERMODYNAMICAL RELATIONS IN SIMPLE AND IN COMPLEX SYSTEMS, BY THE METHODS OF JACOBIAN ANALYSIS

by

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INTRODUCTION

A useful collection of thermodynamical formulas for a single phase one component system of constant mass was given by Bridgman in 1914 (2). A revised version was published in 1925 (3), with the addition of a table for a two phase one component system. In 1930, Goranson (9) published tables for multi-component systems, employing Bridgman's method in amplified form. These tables include the following cases:

(a) all component masses but one constant;

- (b) all component masses but two constant;
- (c) all component masses but three constant:

In 1935, a general method for the derivation of thermodynamical relations in simple systems, making use of elementary properties of Jacobians, was given by Shaw (16). In 1940, Tobolsky (19), apparently unaware of this work, gave another, more cumbersome, method of deriving relations. (A comparison of the two methods, by means of examples, is given in Appendix 1.)

In the present paper, the methods of Jacobian analysis are extended to systems determined by more than two independent variables. A detailed analysis is given for systems of type (a) treated by Goranson, consideration of which was begun previously by the

(**i**i)

author in his Master's thesis (/3). Brief treatments are given of cases (b) and (c).

Following the line of approach given in Table Ia of Shaw's paper for dealing with a particular equation of state, a large number of proposed equations are grouped under some general headings, with information provided for the ready evaluation of derivatives associated with any given equation.

A systematic treatment is given for the derivation of relations on the assumption of an equation of state and the first law of thermodynamics.

Further simplification in the transformation of second derivatives for two variable systems is achieved by the use of second order differentials. A number of simple second derivative relations are also obtained by the methods used for first derivatives.

Some miscellaneous topics are considered in the appendices: Tobolsky's method, a proof of the restricted Le Chatelier-Braun Principle using Jacobians, two phase two component systems, and applications of matrix notation.

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SUMMARY

The following résumé indicates the material covered in the various chapters and appendices: Chapter 1: The methods of Jacobian analysis are extended to systems determined by three independent variables, a detailed treatment being given for the case of a system in which all component masses but one are constant. Tables are provided which simplify considerably the problem of deriving relations between first partial derivatives for systems of this type.

Chapter 2: The same methods are applied to systems determined by (a) four, and (b) five, independent variables, brief treatments being given for systems in which (a) all component masses but two are constant, (b) all component masses but three are constant.

Chapter 3: To illustrate the use of Jacobians in other thermodynamical systems, a brief review is given of the thermodynamics of magnetization. Part (A) is a summary of Stoner's analysis (17), with indications of the use of the methods developed in Chapter 1. In Part (B), methods previously given for simple systems (16) are directly applied to Guggenheim's analysis (10) for a system at constant configuration.

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Chapter 4: Following the method used in Table Ia of Shaw's paper (%) for particular equations of state, a large number of proposed equations are grouped under some general headings, with information provided for the ready evaluation of derivatives, or determination of relations associated with any particular equation. The Tables also simplify the problem of comparing the values of a given derivative obtained from different equations of state. Chapter 5: A systematic treatment is given for deriving relations requiring only the assumption of an equation of state and the first law of thermodynamics. Chapter 6: Second order differentials, combined with the methods of Jacobian analysis, are used to achieve further simplification in the transformation of second derivatives for two variable systems.

In addition, an adaptation of the methods developed for first derivatives is employed in deriving a large number of simple second derivative relations. Appendix 1: By means of examples, a comparison is given of Tobolsky's method for deriving relations, and the methods of Jacobian analysis. Appendix 2: An alternative proof, employing Jacobians,

is given for the restricted Le Chatelier-Braun Principle as enunciated by Epstein (7).

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Appendix 3: The use of Jacobians is indicated for summarizing information pertaining to two phase two component systems.

Appendix 4: Matrix notation is used for writing compactly: (a) the conditions of equilibrium in a heterogeneous system; (b) the differential expressions for the characteristic functions; and (c) a derivation of the Gibbs-Duhem relations for the system.

Appendix 5: This deals with an alternative, but less comprehensive, treatment of the systems described in Chapter 1. The method consists in replacing a three variable system by a set of simple systems, to which are applied previously developed methods of Jacobian analysis. (vii)

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Chapter 1.

Variable Mass Systems: All masses but one constant.

The purpose of this chapter is to extend the methods of Jacobian analysis previously developed for simple systems (14), to the case of a system determined by three independent variables; in particular, to a variable mass system in which all masses but one are constant. Tables for such a system have been published by Goranson (9); by their use, a given first derivative is expressed in terms of derivatives in which pressure, temperature, and the variable mass component are the independent variables. Derivatives involving the chemical potential are not included in these tables; however, a number of such relations is given in his table of second derivatives.

We shall find that, by the methods of Jacobian analysis, the relations given by Goranson are readily verified; derivatives involving the chemical potential are as easily handled; and a given derivative can be transformed quite simply into a set of derivatives containing any specified set of independent variables (not necessarily pressure, temperature, and the variable mass component). Further, the investigation of relations among given sets of derivatives is considerably simplified.

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The mathematical relations between derivatives and Jacobians, and the properties of Jacobians, will not be developed here. A brief account of the properties most useful in the present work will be found in (13).

Consider a homogeneous system consisting of n chemical species S_1 , S_2 ,... S_n , having masses m_1 , m_1 , ... m_n ; and let all masses be kept constant with the exception of m_{κ} , the mass of component S_{κ} . The differential expression for the energy of the system is:

 $dE = TdS - pdv + \mu_{\kappa} dm_{\kappa}$ (1) where μ_{κ} is the chemical potential of component S_{κ} . The definitions of the other characteristic functions lead to the differential expressions:

 $dH = TdS + vdp + \mu_{\kappa}dm_{\kappa}$ (2) $dF = -SdT - pdv + \mu_{\kappa}dm_{\kappa}$ (3) $dG = -SdT + vdp + \mu_{\kappa}dm_{\kappa}$ (4)

where H is the enthalpy, F the Helmholtz free energy, and G the Gibbs function.

Four additional characteristic functions can be defined as follows:

 $E_{2} = E - \mu_{\kappa} m_{\kappa}$ $H_{2} = H - \mu_{\kappa} m_{\kappa}$ $F_{2} = F - \mu_{\kappa} m_{\kappa}$ $G_{2} = G - \mu_{\kappa} m_{\kappa},$

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with corresponding differential expressions:

dE2 = TdS - pdv - m _k dµ _k	• • • • • • • • • • • • • • • • • • • •	(5)
$dH_{2} = TdS + vdp - m_{\kappa}d\mu_{\kappa}$	• • • • • • • • • • • • • • • • • • • •	(6)
$dF_{2} = -SdT - pdv - m_{\kappa}d\mu_{\kappa}$	•••••	(7)
$dG_2 = -SdT + vdp - m_{\kappa}d\mu_{\kappa}$	• • • • • • • • • • • • • • • • • • • •	(ර්)

It will be noted that μ_{κ} is an independent variable for these functions, analogous to the role played by m_{κ} in equations (1) - (4). There does not appear to be any immediate practical application of these functions; however, in the case of other systems determined by three independent variables, functions analogous to the above are found to be of use (e.g. in the thermodynamics of magnetization as treated by Stomer (17)). For the present purpose, we shall find shortly that one of the reciprocity relations obtained from any one of the equations (5) to (8) yields a simple equality between Jacobians not easily obtained from equations (1) to (4).

In Jacobian notation, the above equations become: $J(E, x, y) = TJ(S, x, y) - pJ(v, x, y) + \mu_{K}J(m_{K}, x, y) \quad (9)$ $J(H, x, y) = TJ(S, x, y) + vJ(p, x, y) + \mu_{K}J(m_{K}, x, y) \quad (10)$ $J(F, x, y) = -SJ(T, x, y) - pJ(v, x, y) + \mu_{K}J(m_{K}, x, y) \quad (11)$ $J(G, x, y) = -SJ(T, x, y) + vJ(p, x, y) + \mu_{K}J(m_{K}, x, y) \quad (12)$ $J(E_{2}, x, y) = TJ(S, x, y) - pJ(v, x, y) - m_{K}J(\mu_{K}, x, y) \quad (13)$ $J(H_{2}, x, y) = TJ(S, x, y) + vJ(p, x, y) - m_{K}J(\mu_{K}, x, y) \quad (14)$

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expressions (1) to (2) are exact differentials.

Thus from equation (1):

$$(\partial T/\partial v)_{S,m_{K}} = -(\partial p/\partial S)_{v,m_{K}};$$

$$(\partial T/\partial m_{K})_{S,v} = (\partial \mu_{K}/\partial S)_{v,m_{K}};$$

$$- (\partial p/\partial m_{K})_{S,v} = (\partial \mu_{K}/\partial v)_{S,m_{K}};$$

$$= J(p,v,m_{K}) = J(T,S,m_{K});$$

$$J(p,v,S) = -J(v,\mu_{K},m_{K});$$

$$J(p,v,S) = J(S,\mu_{K},m_{K});$$

$$A_{4} = Z_{2};$$

$$X_{1} = -K_{2};$$

whence

i.e.

 $A_1 = K_4$. The equality $A_3 = Z_1$ is most easily obtained from any one of equations (5) - (8).

Table 2 has been constructed for the following purpose: For a particular choice of independent variables q,r,t, the corresponding Jacobian J(q,r,t) = 1. The evaluation of J(x,y,z), when x,y,z are none of q,r,t, is then somewhat complicated. By expressing J(x,y,z) in terms of other Jacobians, this difficulty is removed. For example, if J(p,v,T) = 1, the occurrence of $J(S,\mu_K,m_K)$; i.e., K_{ϕ} , is avoided by use of the relation $K_{\phi} = A_2$. All cases that may be encountered are summarized in Table 2. The lengthier entries are deduced from relations among the reference quantities to be derived subsequently. The table is used as follows: if any symbol in column 1 is equal to 1, the corresponding symbol in column 2 is avoided by use of the equivalent expression in column 3.

Construction of Tables 3 and 3a.

We now turn to Tables 3 and 3a, the construction of which is based on the direct application of equations (9) to (16). Jacobians involving only one of the characteristic functions are expressed in terms of the reference Jacobians by substituting for x and y any two of $p,v,T,S,\mu_{\kappa}, m_{\kappa}$. Those involving two or more of the characteristic functions are similarly resolved by making use of the portions of the tables already completed.

 $\underline{\text{Ex. 1}} \quad J(\text{H}, \text{v}, \text{T}) = \text{TJ}(\text{S}, \text{v}, \text{T}) + \text{vJ}(\text{p}, \text{v}, \text{T}) + \mu_{\kappa} J(\text{m}_{\kappa}, \text{v}, \text{T}) = \text{TX}_{1} + \text{vA}_{1} + \mu_{\kappa} X_{3}$ $\underline{\text{Ex. 2}} \quad J(\text{G}, \text{E}, \text{T}) = -\text{SJ}(\text{T}, \text{E}, \text{T}) + \text{vJ}(\text{p}, \text{E}, \text{T}) + \mu_{\kappa} J(\text{m}_{\kappa}, \text{E}, \text{T})$ $= -\text{v}(\text{TB}_{1} + \text{pA}_{1} + \mu_{\kappa} B_{3}) - \mu_{\kappa} (\text{TZ}_{2} + \text{pX}_{3}).$

Table 3 involves the functions $\mathbb{E}, \mathbb{H}, \mathbb{F}, G$; Table 3a provides a similar summary for the less frequently encountered functions $\mathbf{E_2}, \mathbb{H_2}, \mathbb{F_2}, \mathbb{G_2}$. The value of J(x, y, z), for any x given in the left-hand column and any y, z given in the top row, is found at the intersection of the specified row and column.

Relations among Reference Jacobians.

Before discussing applications of Table 3, we shall

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consider briefly the relations that exist among the various reference Jacobians. If $x_0, x_1, x_2, x_3, z_1, z_2$, are a set of admissible variables, eight Jacobians corresponding to this particular selection are related by the equation: $J(x_0, x_1, x_2) J(x_3, z_1, z_2) - J(x_1, x_2, x_3) J(x_0, z_1, z_2)$ $+J(x_2, x_3, x_0) J(x_1, z_1, z_2) - J(x_1, x_0, x_1) J(x_2, z_1, z_2) = 0 \dots$ (A) However, it will be found more useful to have a relation involving, in general, only six Jacobians. This can be obtained from (A) by setting, for example, $x_0 = z_2$. We then have (with a slight change of notation): $J(x, y, u) \cdot J(z, t, u) + J(y, z, u) \cdot J(x, t, u) + J(z, x, u) \cdot J(y, t, u) = 0 \dots$ (B) <u>Example</u>. Setting x = p; y = v, z = T; t = S; $u = m_K$, we obtain:

 $J(p, v, m_{\kappa}) J(T, S, m_{\kappa}) + J(v, T, m_{\kappa}) J(p, S, m_{\kappa}) + J(T, p, m_{\kappa}) J(v, S, m_{\kappa}) = 0;$ i.e. $A_{4}^{2} + K_{3}C_{2} - B_{3}Y_{2} = 0.$

This equation is, in fact, the one to be used in the derivation of relations for a simple (constant mass) system (compare with the equation in Shaw's paper, $b^2 + ac - ln = 0$, to which it corresponds).

By assigning different sets of values to x,y,z,t,u a large number of relations is obtained. Several of these are summarized in Table 4. With u equal to one of p,v,T, $S,\mu_{\kappa},m_{\kappa}$, the number of sets of values of x,y,z,t, is equal to 5; i.e. to a definite value of u correspond five equations. Thus thirty equations are obtained in groups of five.

Equation (B) was also used in the derivation of the lengther entries of Table 2.

Applications

A direct and particularly useful application of Tables 3 and 3a consists in expressing a given partial derivative in terms of other derivatives containing any chosen set of independent variables. For example, if p,T,m_{K} are chosen as independent variables, a given derivative can be readily transformed into a group of derivatives for which the independent variables are p,T,m_{K} .

Tables giving information of this particular type have been published by Goranson (9); these are restricted by not including derivatives involving μ_{κ} . Table 3 yields, without any difficulty, all the results given in Goranson's Groups 9 to 36, and provides data for the evaluation of derivatives involving μ_{κ} . Further any other choice of independent variables can be made, by setting the appropriate Jacobian equal to 1. Hence a given derivative is readily expressible in terms of partial derivatives for which the independent variables are any chosen set x,y,z. Except for the case where the independent variables are p,T,m_k, such results are not, in general, directly obtainable from tables of partial derivatives hitherto published.

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The above remarks apply also to Table 3a, which is used in transforming derivatives of E_2, H_2, F_2, G_2 .

<u>Ex. 1</u> Express $(\partial F/\partial p)_{\tau,s}$ in terms of derivatives for which the independent variables are:

(a)
$$p,T,m_{\kappa}$$
; (b) v,S,m_{κ} .

(a) (Goranson, Group 12, p. 177) Here
$$B_3 = 1$$
.
 $(\partial F/\partial p)_{T,S} = (-pX_1 + \mu_K Z_2)/B_1$
 $= \frac{-p[(\partial v/\partial p)(\partial S/\partial m_K) - (\partial v/\partial m_K)(\partial S/\partial p)] + \mu_K(\partial v/\partial T)}{(\partial S/\partial m_K)}$

Since $(\partial S/\partial p)_{\tau, m_{\kappa}}$ is not one of the standard derivatives employed by Goranson, we may substitute for it the equivalent $-(\partial v/\partial T)_{\sigma, m_{\kappa}}$ obtained from the equality $A_{\mu} = \mathbb{Z}_{2}$.

(b) Here
$$Y_2 = J(v, S, m_\kappa) = 1$$
.
 $(\partial F/\partial p)_{T,S} = (-pX_1 + \mu_\kappa Z_2)/B_1$
 $= \frac{p(\partial T/\partial m_\kappa) - \mu_\kappa (\partial p/\partial S)}{-(\partial p/\partial v)(\partial T/\partial m_\kappa) + (\partial p/\partial m_\kappa)(\partial T/\partial v)}$

on dividing numerator and denominator by Y_2 , and evaluating the resulting ratios of Jacobians.

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In the above answers, subscripts indicating the quantities held constant in the several derivatives have been dropped, since they are sufficiently clear from the context. <u>Ex. 2</u> Express $(\partial T/\partial p)_{H,v}$ in terms of derivatives for which v,T,m_K are the independent variables. $(\partial T/\partial p)_{H,v} = J(H,T,v)/J(H,p,v) = -(TX_1 + vA_1 + \mu_{\kappa}X_3)/(TA_2 + \mu_{\kappa}A_4).$

Dividing numerator and denominator by $X_3 = J(v, T, n_{\kappa})$ and evaluating the resulting ratios of Jacobians, we obtain:

$$(\partial T/\partial p)_{H,v} = - \frac{T(\partial S/\partial m_{\kappa}) + v(\partial p/\partial m_{\kappa}) + \mu_{\kappa}}{T[(\partial p/\partial m_{\kappa}) (\partial S/\partial T) - (\partial p/\partial T) (\partial S/\partial m_{\kappa})] - \mu_{\kappa} (\partial p/\partial T)}$$

$$\frac{Ex. 3}{Express} \left(\partial \mu_{\kappa} / \partial p \right)_{H,m_{\kappa}} \text{ in terms of derivatives for which}$$

$$p,T,m_{\kappa} \text{ are the independent variables. (Goranson, Group 7, p. 270). }$$

This example illustrates how derivatives involving μ_{κ} are as easily handled as derivatives involving other quantities. Goranson treats this as a second derivative problem.

$$(\partial \mu_{\kappa} / \partial p)_{H,m_{\kappa}} = (TK_{4} + vK_{1}) / (-TC_{2})$$

$$= (TA_{2} - vB_{1}) / (-TC_{2})$$

$$= \frac{T \left[(\partial v / \partial T) (\partial S / \partial m_{\kappa}) - (\partial v / \partial m_{\kappa}) (\partial S / \partial T) \right] - v (\partial S / \partial m_{\kappa})}{-T(\partial S / \partial T)}$$

$$= (\partial v / \partial m_{\kappa}) + (\partial S / \partial m_{\kappa}) \left[v - T(\partial v / \partial T) \right] / (\partial S / \partial T) .$$

<u>Ex. 4</u> Express $(\partial E/\partial T)_{e,\mu\kappa}$ in terms of derivatives containing v,T,m_k as independent variables.

$$(\partial E/\partial T)_{\theta,\mu_{K}} = (-TC_{1} + pA_{3} + \mu_{K}K_{1})/(-B_{2}).$$

= $[-T(B_{2}Y_{2} + B_{1}X_{1} - A_{3}A_{4})/X_{3} + pA_{3} - \mu_{K}B_{1}]/(-B_{2})$

where C_1 has been replaced by its equivalent in Table 2. For $J(v,T,m_k)=X_3=1$, the numerator of the expression on the right is: $-T\left[\left(\frac{\partial p}{\partial v}\right)\left(\frac{\partial \mu_{\kappa}}{\partial m_{\kappa}}\right) - \left(\frac{\partial p}{\partial m_{\kappa}}\right)\left(\frac{\partial \mu_{\kappa}}{\partial v}\right)\right] \left(\frac{\partial \beta}{\partial T}\right) \\ - \left(T\left(\frac{\partial S}{\partial m_{\kappa}}\right) + \mu_{\kappa}\right)\left[\left(\frac{\partial p}{\partial v}\right)\left(\frac{\partial S}{\partial m_{\kappa}}\right) - \left(\frac{\partial p}{\partial m_{\kappa}}\right)\left(\frac{\partial S}{\partial v}\right)\right] \\ + \left(p - T\left(\frac{\partial p}{\partial T}\right)\left[\left(\frac{\partial p}{\partial m_{\kappa}}\right)\left(\frac{\partial \mu_{\kappa}}{\partial T}\right) - \left(\frac{\partial p}{\partial T}\right)\left(\frac{\partial \mu_{\kappa}}{\partial m_{\kappa}}\right)\right] \dots (a) \\ \text{The denominator is:}$

 $(\partial p/\partial m_{\kappa})(\partial \mu_{\kappa}/\partial v) - (\partial p/\partial v)(\partial \mu_{\kappa}/\partial m_{\kappa})$ (b) The equivalent expression for $(\partial E/\partial T)_{\theta,\mu_{\kappa}}$ is then given by the ratio of (a) to (b).

Derivatives of this type (in which $\mu_{\mathbf{k}}$ is/independent variable) are not given in Goranson's Tables.

Applications of Table 4.

<u>Ex. 5</u> By analogy with the formula for the difference of the specific heats in a simple system, we wish to investigate the difference between $(\partial S/\partial T)_{\ell,\mu_{k}}$ and $(\partial S/\partial T)_{\nu,\mu_{k}}$. We note that μ_{k} is held constant in both derivatives, and that the remaining variables are p,v,T,S. Referring to Table 4, we find the appropriate equation to be:

$$A_3^2 + X_2C_1 - B_2Y_1 = O$$

We then have:

$$(\partial \mathbb{B}/\partial \mathbb{T})_{\theta,\mu_{K}} - (\partial \mathbb{B}/\partial \mathbb{T})_{\psi,\mu_{K}} = (\mathbb{C}/\mathbb{B}_{2}) - (\mathbb{Y}/\mathbb{H}_{2})$$
$$= (\mathbb{X}_{2}\mathbb{C}_{1} - \mathbb{B}_{2}\mathbb{Y}_{1})/\mathbb{B}_{2}\mathbb{X}_{2}$$
$$= \mathbb{A}_{3}^{2}/\mathbb{B}_{2}\mathbb{X}_{2}$$
$$= -(\partial \mathbb{V}/\partial \mathbb{T})_{\theta,\mu_{K}} \cdot (\partial \mathbb{P}/\partial \mathbb{T})_{\psi,\mu_{K}}.$$

Further, by the methods developed in this chapter, the above result can be transformed into other derivatives containing any specified set of independent variables. E. 6 Find a relation among $(\partial v / \partial r)_{m_{K},p}$, $(\partial / \partial S)_{\mu_{K},p}$, $(\partial Z / \partial - \kappa)_{v_{J}p}$, $(\partial \varphi_{K} / \partial m_{K})_{S,p}$, $(\partial \omega_{K} / \partial v)_{m_{K},p}$, and, if necessary, other derivatives.

$$(\partial \nabla / \partial G)_{m_{\kappa,\beta}} = A_{4} / G_{2}$$

$$(\partial \nabla / \partial G)_{m_{\kappa,\beta}} = A_{3} / G_{1}$$

$$(\partial \nabla / \partial G)_{\mu_{\kappa,\beta}} = A_{3} / G_{1}$$

$$(\partial E_{1} / \partial -_{\kappa})_{\nu,\rho} = (E_{12} + \mu_{\kappa} \wedge_{4}) / A_{4}$$

$$(\partial F_{\kappa} / \partial -_{\kappa})_{s,\rho} = C_{1} / C_{2}$$

$$(f)$$

$$(\partial F_{\kappa} / \partial \nabla)_{m_{\kappa,\beta}} = Y_{1} / A_{4} = -B_{1} / A_{4}$$

$$(f)$$

Inspection of the above equations shows that the only reference Jacobians involved are $A_2, A_3, \dots, B_r, C_r, C_2$. From Table 4, the appropriate relation is:

The reference Jacobians are readily eliminated from equations (1) to (5) and a relation among the five derivatives obtained, no additional derivatives being required.

Thus:

$$A_{4} = (\partial \nabla / \partial S)_{m_{K,\beta}} \cdot C_{2}$$

$$C_{1} = (\partial \mu_{K} / \partial \mu_{K})_{S,\beta} \cdot C_{2}$$

$$A_{3} = (\partial \nabla / \partial S)_{\mu_{K,\beta}} \cdot (\partial \nabla / \partial S)_{K,\beta} \cdot C_{2}$$

$$B_{1} = -(\partial \mu_{K} / \partial \nabla)_{m_{K,\beta}} \cdot (\partial \nabla / \partial S)_{m_{K,\beta}} \cdot C_{2}$$

$$A_{2} = (1/T) \left[(\partial E / \partial \mu_{K})_{\sigma,\beta} - \mu_{K} \right] (\partial \nabla / \partial S)_{m_{K,\beta}} \cdot C_{2} \cdot C_{2}$$
Substituting in (6):

 $(1/T) \left[(\partial \Xi \langle \partial_{\kappa} \rangle_{\sigma, \theta} - \mathcal{H}_{\kappa} \right] \cdot (\partial_{m\kappa} \langle \partial \nabla \rangle_{m\kappa, \theta} \cdot (\partial \nabla \langle \partial \Xi \rangle_{m\kappa, \theta}^{2} + (\partial \nabla \langle \partial \Xi \rangle_{m\kappa, \theta}^{2} \times (\partial \mathcal{H}_{\kappa, \theta} \langle \partial \nabla \rangle_{m\kappa, \theta} \times (\partial \nabla \langle \partial \Xi \rangle_{m\kappa, \theta} \times (\partial \nabla \langle \partial \Xi \rangle_{m\kappa, \theta} \cdot (\partial \nabla \langle \partial \Xi \rangle_{m\kappa, \theta} \times (\partial \nabla \langle \partial \Sigma \rangle_{m\kappa, \theta} \times (\partial \nabla \langle \partial \Xi \rangle_{m\kappa, \theta}$

Summary: In view of the variety of topics mentioned, we present a summary of the main points:

(1) The Tables of First Derivatives given by Goranson (Groups 9 to 36) transform a given derivative into other derivatives containing p,T,m_{κ} as independent variables. Derivatives involving μ_{κ} are not treated in these groups; they can be divided into two types:

(a) those expressible in terms of the reference Jacobians

 $K_1, K_2, K_3, K_4;$

(b) those expressible in terms of $A_2, B_2, C_1, X_2, Y_1, Z_1$.

Some relations of type (a) are given in Goranson's Table of Second Derivatives (Table II, Groups 1 to 8, last expression in each group). Relations of type (b) are not treated by Goranson.

(2) (a) The methods of Jacobian analysis, together with Table 3, provide a simple means of verifying or independently deriving the relations given by Goranson.

(b) A given derivative is readily expressed in terms of other derivatives containing any chosen set of independent variables.

(c) Derivatives involving $\mu_{\boldsymbol{K}}$ are as easily handled as the others.

(d) The use of Table 4 simplifies the problem of investigating relations among derivatives for which the independent variables are not too dissimilar. (3) Characteristic functions are defined, in addition to those commonly used. Although they do not seem to have any practical significance for variable mass systems, functions analogous to them are of importance in other three variable systems.

$J(S, u_1, m_1) = \kappa_1$		= -K ₉	$A_3 = Z_1 \qquad X_1$
$J(T, \mu_k, m_k) = K_{\overline{J}}$	$J(T, S, m_k) = Z_2$	••••••••••••••••••••••••••••••••••••••	$A_1 = K_3$ $A_2 = K_4$
	$J(T, S, \mu_k) = Z_1$		EQUALITIES:
$J(v, \mu_k, m_k) = K_2$	$J(v, S, m_K) = Y_2$	$J(v, T, m_k) = X_z$	
	$J(v, S, \mu_{k}) = Y_{1}$	$J(v, T, \mu_k) = X_2$	
		$J(v, T, S) = X_1$	
$J(p, \mu_k, m_k) = K_1$	$J(p, S, m_k) = C_2$	$J(p, T, m_k) = B_3$	$J(p, v, m_k) = A_{\downarrow}$
	$J(p, S, \mu_k) = C_1$	$J(p, T, \mu_k) = B_2$	$J(p, v, \mu_k) = \Lambda_3$
		J(p, T, S) = B ₁	$J(p, v, S) = A_2$
		γ.	$J(p, v, T) = A_1$
	s and Their Symbols	of Reference Jacobian	List
ana parawar 1 May 1999 (Ar-Johnson), Pangalar 1990 (Kana ang ang ang ang ang ang ang ang ang		TABLE	

х,

Byl + AlAs - BlXl	B2	XS
T _A		
B ₂ Y ₂ + B ₁ X ₁ - A ₁ A ₂	۶ _ط	τ _λ
B2Y2 + B1X1 - A3Alt	τ _ρ	٤ _X
S ^X		
$\pi_{Y} \xi_{Y} - \tau_{X} \tau_{H} - \tau_{X} \xi_{H}$	^ر ی	2X X
τ _g -	τ_X	τ _x
٥S		
t _I y - τ _X τ _E - τ _X ξ _E	Xp	C D
G	ĘŢ	To
t ^A F ^A - L ^X L ^E + S ^Y S ^E	-X	-5
£ 8	- т	с
B ₂ Y ₂ + B ₁ ^X 1 - A ₁ A ₂	٦	B
ع	21	ی 2 ⁰
SDZ + SUA		C.
T _X -	K2	ВТ
٤ _V	τ _z	+(A
$+_{7V}$	S ^Z	٤ _٣
$\tau_{ abla}$	٤X	S ^A
S ^A	K1+	τ _Ψ
E	S	τ
(T,T,T) atios of the Type $\overline{\mathbf{J}(\mathbf{x},\mathbf{y},\mathbf{z})}$	noitenimilA	
TABLE 2	ar a "aparte latit dalam den den a s'anna filma (latit e second de da de	



Use of Table

If Jacobian in column l is equal to l, avoid occurrence of adjacent Jacobian in column 2 by using equivalent express

	<u>y</u>			רי גי	чк К	01	' J		U I	try
-SA1+h ^K Alt	-SA1+hkyah	TA2+µkA11	TA2+μ _K Aμ	Alt	Az	A2	Al	0	0	٨đ
$\begin{array}{ccc} \mathrm{SB}_1 + \mathrm{pA}_2 & \mathrm{SB}_2 + \mathrm{pA}_2 \\ \mathrm{pA}_1 + \mathrm{\mu}_k \mathrm{B}_3 & + \mathrm{\mu}_k \mathrm{C}_2 & + \mathrm{\mu}_k \mathrm{K}_1 \\ \mathrm{\mu}_k \mathrm{B}_3 & \mathrm{SB}_1 + \mathrm{\mu}_k \mathrm{C}_2 & \mathrm{SB}_2 + \mathrm{\mu}_k \mathrm{K}_1 \end{array}$		TB1+μkB3	TB1+pA1	B	B2	B	0	-A1	0	рT
		μ _k C2	pA2+µkC2	C2	C ₁	0	۰ B ₁	-A ₂	0	PS PS
		-TC1+µkK	-TC1+PA3 +µ _K K1	КŢ	0	- C 1	- Bဥ	-A3	0	ppk
S B S B S B S B S B S B S B S B S B S B	-TQ +PA4		-102- -2011-	0	-K1	-0 ₂	-в ₃	-A14	0	pm _k
vA1+µkX3	μ _X X3	$\frac{TX_1 + vA_1}{+ \mu_k X_3}$	TX1+µkX3	£X	X2	X1	0	0	A ₁	vT vT,y,
SX1+VA2 +µ _K Y2	SX1+mkY2	vA2+mkY2	μκΥ2	¥2	Υ ₁	0	TX-		Ă	
SX2+VA3 +µK2	SX2+µ _K K2	-TY1+vA3 +µ _k K2	-TY1+µ _K K2	K2	0	-Y_	-X2	Ο	A ₃	$v\mu_k$
^{SX} 3 + v ^A 4	ξxs	-TY2+vA4	-TY2	0	-K2	-Y ₂	-X3	0	μ	vm _k

1	Ω	μ	н		H	mĸ		p.,	M	H	4	q	x y,3 +	
	$\begin{split} & \mathbb{P}\left[\mathbb{VSB}_{l} + \mathbb{P}(SX_{l} + \mathbb{VA}_{2} + \mathbb{P}_{K}Y_{2}) + \mathbb{VP}_{K}C_{2} \right] \\ & + \mathbb{P}\mathbb{VSA}_{l} + S\mathbb{P}_{K}(\mathbb{VB}_{3} + \mathbb{P}X_{3}) \end{split}$	0	0	+ $vSA_1 + S\mu_K X_3 - vS\mu_K B_3$	$- \mathbf{\nabla} \mathbb{T} \big(\operatorname{SB}_{\boldsymbol{i}} + p \operatorname{A}_{\boldsymbol{\lambda}} + \mathfrak{p}_{\boldsymbol{\kappa}} \operatorname{C}_{\boldsymbol{\lambda}} \big) - p \left[\mathbb{T} \big(\operatorname{SX}_{\boldsymbol{i}} + \mathfrak{p}_{\boldsymbol{\kappa}} \operatorname{Y}_{\boldsymbol{\lambda}} \big) \right]$	$T(SZ_{2}+pY_{2})-v(SB_{3}+pA_{4})$	$-\mu_{\kappa}(SK_{3}+pK_{2})$	$\mathbb{T}(SZ_1 + pY_1 - \mu_{\mathbf{K}}K_{4}) - \nabla(SB_{2} + pA_{3} + \mu_{\mathbf{K}}K_{1}) - \nabla(SB_{2} + \mu_{\mathbf{K}}K_{1}) - \nabla(SB_{1} + \mu_{$	$-\nabla(SB_i + pA_2 + \mu_{\kappa}C_2) - \mu_{\kappa}(SZ_2 + pY_2)$	$-\mathbb{T}(p\mathbb{X}_{I}-\mu_{K}\mathbb{Z}_{2})-\mathbb{V}(p\mathbb{A}_{I}+\mu_{K}\mathbb{B}_{3})-p\mu_{K}\mathbb{X}_{3}$	$T(SX_1 + \mu_K Y_2) + v(SA_1 - \mu_K A_4) + S\mu_K X_3$	$T(SB_1 + pA_2 + \mu_K C_2) + \mu_K (SB_3 + pA_W)$	ΗF	
	0	$-T\left[vSB_{i}+p(SX_{i}+vA_{2}+\mu_{K}Y_{2})+v\mu_{K}C_{2}\right]$ $-pvSA_{i}-S\mu_{K}(vB_{3}+pX_{3})$	0	$+ \operatorname{Sp}_{\boldsymbol{k}} \mathbb{X}_{\boldsymbol{j}} - \operatorname{Vp}_{\boldsymbol{k}} (\operatorname{TC}_{\boldsymbol{\lambda}} + \operatorname{SB}_{\boldsymbol{j}})$	$-\nabla TSB_{1} - p \Big[T (SX_{1} + vA_{2} + \mu_{K} Y_{1}) + vSA_{1} \Big]$	$T(SZ_2 - VC_2) - VSB_3$		$\mathbb{T}(\mathbb{SZ}_{l} - \mathbb{VC}_{l} - \mathbb{P}_{k}\mathbb{K}_{4}) - \mathbb{VSB}_{2} - \mathbb{SP}_{k}\mathbb{K}_{3}$	-S(VB+p,Zz)	$T(vB_{l}+\mu_{\kappa}Z_{2})$	$T(SX_{i} + vA_{2} + \mu_{\kappa}Y_{i}) + vSA_{i} + S\mu_{\kappa}X_{3}$	T(SB,+µ _K C ₂)+Sµ _K B ₃	ΗG	TABLE 3. (cont'd)
	0	0	$\begin{split} & \mathbb{T}\left[\mathbb{VSB}_{i} + \mathbb{P}\left(SX_{i} + \mathbb{VA}_{2} + \mathbb{P}_{K}Y_{2} \right) + \mathbb{VP}_{K}C_{2} \right] \\ & + \mathbb{P}\mathbb{VSA}_{i} + \mathbb{SP}_{K}\left(\mathbb{VB}_{j} + \mathbb{P}X_{j} \right) \end{split}$	+ $pvSA_1 + Sp_k(vB_3 + pX_3)$	$\mathbb{T}\left[\mathbb{VSB}_{i} + \mathbb{P}\left(SX_{i} + \mathbb{VA}_{\lambda} + \mu_{k}Y_{\lambda}\right) + \mathbb{V}\mu_{k}C_{\lambda}\right]$	$vSB_3 + p(SX_3 + vA_4)$		$vSB_{2}+p(SX_{2}+vA_{3}+\mu_{K}X_{2})+v\mu_{K}X_{I}$	$\nabla SB_{l} + p(SX_{l} + vA_{2} + \mu_{\kappa}Y_{2}) + v\mu_{\kappa}C_{2}$	$p(vA_1 + \mu_K X_3) + v\mu_K B_3$	$-v(SA_{1}-\mu_{K}A_{4})$	$p(SA_i - \mu_K A_F)$	FG	