

MEMORANDUM

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**SPECIFICATIONS FOR
A NEW JACOBIAN PACKAGE FOR THE
RAND CHEMICAL EQUILIBRIUM PROGRAM**

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PREFACE

This Memorandum is one of a series of RAND publications dealing with computational questions in connection with the program developed at RAND to solve chemical composition problems. In this publication the authors describe routines for obtaining markedly improved and expanded sets of Jacobian matrices pertaining to a chemical problem. These matrices consist of partial derivatives of various dependent variables with respect to various independent parameters important in establishing the composition of a chemical system. For many problems, the use of these Jacobian matrices, combined with very little hand computation, can yield good approximations to new compositions resulting from changes in state-determining parameters.

The chemical program and the Jacobian matrices have played an important role in the study of the chemistry of physiological systems. They have also been used in other fields where computational analyses of complex chemical systems are necessary, such as in studies of rocket propulsion systems, planetary atmospheres, and reentry problems.

ABSTRACT

This Memorandum contains specifications for a new Jacobian package intended for use with RAND's chemical equilibrium program.

The new package has a much greater scope than the earlier version in that it (1) provides for computation of Jacobians that reflect changes not only in amounts of input and in the free energy parameters, as in the earlier package, but also in the detached coefficients of the mass balance matrix and in all of the components of a given species; (2) permits selection of one, a few, or all of the partial derivatives of any of the above kinds; and (3) permits evaluation of the effect of these changes not only on the mole number, compartment totals, and mole fractions of the solution, but also on logarithmic versions of these variables.

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1. INTRODUCTION

This Memorandum describes and gives instructions for using a new and improved Jacobian package. The package consists of a group of subroutines to be used with RAND's chemical equilibrium program.

The Jacobian matrices that the package computes consist of partial derivatives of certain quantities in the solution of a model (dependent variables) with respect to certain parameters in the model (independent variables). By using these derivatives one can predict how a change in a model parameter can affect the model solution, and, in many cases, the user can obtain a good approximation for how much effect a certain type of change will have without re-solving the problem. One might use them, for example, to see how much the pH of a model changes with an increase in the pressure of CO_2 , or with an increase in the amount of NaOH, etc.

The predictive ability of the partial derivatives is good only locally--that is, for values relatively close to the solution of the model preceding the use of the package. For large changes it is better to change the inputs of the problem and re-solve rather than to rely on the Jacobians. In physiological applications, large normally means outside the physiological range of changes.

This new package has a much greater scope than the earlier version in that it

- o Provides for computation of Jacobians that reflect changes not only in amounts of input and in the free energy parameters, as in the earlier package, but also in the detached coefficients of the mass balance matrix (for example, in valences) and in all of the components of a given species.

- o Permits selection of one, a few, or all of the partial derivatives of any of the above kinds.
- o Permits evaluation of the effect of these changes not only on the mole number, compartment totals, and mole fractions of the solution, but also on logarithmic versions of these variables. The logarithmic versions indicate fractional rate of change.

Before giving a detailed description of the working of the program, we shall briefly review the meanings of the terms used and illustrate them as they occur in a sample model--a soda pop model.

2. DEFINITION OF TERMS

The terminology used here is the same as that used in previous discussions of RAND's chemical equilibrium program. The structure of the sample model, the soda pop model, is shown in Fig. 1. Figure 2 is the listing of the problem by the chemical equilibrium program, and Fig. 3 is the valid solution by the program. We shall refer to these figures in our definition of terms.

2.1. Compartments, Substances, and Species

The chemical system consists of one or more phases, called compartments. Each compartment contains one or more substances. Each substance in each compartment is called a species. The same substance may exist in more than one compartment; the substances are then considered as different species. The species are the columns of what is called the A matrix. Referring to Fig. 1, we see that this model has two compartments, GAS and LIQUID. The GAS compartment contains four species, O_2 , CO_2 , N_2 , and H_2O . The LIQUID compartment contains 13

$A_{i,j}$ MATRIX

Compartment	GAS	LIQUID	B VECTOR
Substance Species No. j	O_2 1 CO_2 2 N_2 3 H^+ 4 OH^- 5 Cl^- 6 Na^+ 7 K^+ 8 9 Glucose	O_2 5 CO_2 6 N_2 7 H^+ 8 OH^- 9 Cl^- 10 Na^+ 11 K^+ 12 H_2O 13 HCO_3^- 14 H_2CO_3 15 $CO_3^{=}$ 16 Glucose 17	b_i 5.27583 1 6.07349 2 82.5804 3 52.8100 4 52.8395 5 .08005 6 .08813 7 .04829 8 .02000 9
Components	O_2 1 CO_2 1 N_2 1 H^+ 1 OH^- 1 Cl^- 1 Na^+ 1 K^+ 1 9 Glucose	O_2 5 CO_2 6 N_2 7 H^+ 8 OH^- 9 Cl^- 10 Na^+ 11 K^+ 12 H_2O 13 HCO_3^- 14 H_2CO_3 15 $CO_3^{=}$ 16 Glucose 17	b_i 5.27583 1 6.07349 2 82.5804 3 52.8100 4 52.8395 5 .08005 6 .08813 7 .04829 8 .02000 9
c value	0 -7.69 -11.52 -36.6	10.94 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	b_i 5.27583 1 6.07349 2 82.5804 3 52.8100 4 52.8395 5 .08005 6 .08813 7 .04829 8 .02000 9

Fig. 1 — Structure of the Soda Pop Model

SODA POP TEST PROBLEM									
B									
ROWS									
1	O2	5.2758300E 00	-0.	-0.	-0.				
2	CO2	6.0734900E 00	-0.	-0.	-0.				
3	N2	8.2580400E 01	-0.	-0.	-0.				
4	H+	5.2810000E 01	-0.	-0.	-0.				
5	OH-	5.2839500E 01	-0.	-0.	-0.				
6	CL-	8.0050000E-02	-0.	-0.	-0.				
7	NA+	8.8129999E-02	-0.	-0.	-0.				
8	K+	4.8290000E-02	-0.	-0.	-0.				
9	GLUCOSE	2.0000000E-02	-0.	-0.	-0.				
MATRIX									
SPECIES		FREE-ENERGY VALUE			DETACHED COEFFICIENTS AND ROWS				
GAS									
1	O2	-0.000000			1.000 O2				
2	CO2	-7.690000			1.000 CO2				
3	N2	-11.520000			1.000 N2				
4	H2O	-36.600000			1.000 H+	1.000 OH-			
LIQUID									
5	O2	10.940000			1.000 O2				
6	CO2	-0.000000			1.000 CO2				
7	N2	-0.000000			1.000 N2				
8	H+	-0.000000			1.000 H+				
9	OH-	-0.000000			1.000 OH-				
10	CL-	-0.000000			1.000 CL-				
11	NA+	-0.000000			1.000 NA+				
12	K+	2.596600			1.000 K+				
13	H2O	-39.390000			1.000 H+	1.000 OH-			
14	HCO3-	-21.350000			1.000 CO2	1.000 OH-			
15	H2CO3	-32.840000			1.000 CO2	1.000 H+			
16	CO3=	6.260000			1.000 CO2	-1.000 H+			
17	GLUCOS	0.000000			1.000 GLUCOS				
PROBLEM HAS		9 ROWS,	17 COLUMNS,	2 COMPARTMENTS,	24 NON ZERO MATRIX ENTRIES.				

Fig. 2—Listing of Soda Pop Problem

SODA POP TEST PROBLEM

RMS MASS BALANCE ERROR= 9.857E-08 MAX. ERROR= 2.077E-07 ON ROW H+
 RMS EQUILIBRIUM ERROR= 1.899E-07 MAX. ERROR= 3.283E-07 IN CO3= OF LIQUID

VALID SOLUTION

OBJECTIVE= -3.1288600 E 03 RT * OBJECTIVE= -1.9282352 E 06

		GAS	LIQUID
X-BAR		1.00006E 02	4.69702E 01
PH		0.	7.44788E 00
O2	MOLES	5.27579E 00	4.39442E-05
	MFRAC	5.27547E-02	9.35576E-07
CO2	MOLES	6.04274E 00	1.29809E-03
	MFRAC	6.04237E-02	2.76365E-05
N2	MOLES	8.25800E 01	3.85122E-04
	MFRAC	8.25750E-01	8.19929E-06
H2O	MOLES	6.10749E 00	4.67026E 01
	MFRAC	6.10712E-02	9.94302E-01
H+	MOLES	-0.	3.01675E-08
	MFRAC	-0.	6.42269E-10
OH-	MOLES	-0.	5.68544E-07
	MFRAC	-0.	1.21043E-08
CL-	MOLES	-0.	8.00500E-02
	MFRAC	-0.	1.70427E-03
NA+	MOLES	-0.	8.81300E-02
	MFRAC	-0.	1.87630E-03
K+	MOLES	-0.	4.82900E-02
	MFRAC	-0.	1.02810E-03
HCO3-	MOLES	-0.	2.94059E-02
	MFRAC	-0.	6.26053E-04
H2CO3	MOLES	-0.	1.84584E-06
	MFRAC	-0.	3.92982E-08
CO3=	MOLES	-0.	4.67569E-05
	MFRAC	-0.	9.95459E-07
GLUCOS	MOLES	-0.	2.00000E-02
	MFRAC	-0.	4.25802E-04

Fig.3—Solution of the Soda Pop Model by the
 Chemical Equilibrium Program

species, which are listed in Fig. 1. The species (compartment-substance combinations) are numbered in the order of input. Thus O_2 in the GAS compartment is species 1; O_2 in the LIQUID compartment is species 5. There are 17 species in this model. The compartments are also numbered in order of input; GAS is compartment 1 and LIQUID is compartment 2.

2.2. Components

The chemical inputs to the system are called components. Referring to Fig. 1 we see that the model has nine components, which are numbered in the order in which they occur. The components are the rows of the A matrix. The B vector, printed to the right of the A matrix, contains the amounts of the inputs, the b's. In this problem the b's are given in terms of moles. Examples of components are O_2 , which is b_1 and amounts to 5.27583 moles, and N_2 , b_3 which is in the list and amounts to 82.5804 moles. The components are called ROWS in Fig. 2.

2.3. The A Matrix

The A matrix is the mass balance matrix. In the soda pop model it consists of nine rows (components) and 17 columns (species). The entries in the A matrix are the detached coefficients. An entry in the matrix is identified by a component, compartment, and substance name, or component and species number. For example, in Fig. 1, $a_{OH^-, H_2O \text{ in GAS}}$ refers to the entry for which the component is OH^- and the species is H_2O in the GAS compartment. It may also be referred to as $a_{5,4}$ and has a value of 1. Similarly, $a_{CO_2, N_2 \text{ in LIQUID}}$ refers to $a_{2,7}$ and has a value of 0.

2.4. Free Energy Parameters

The free energy parameters are called the c values. There is one for every column of the A matrix, and in Fig. 1 they are listed below the matrix. The c value is identified by a compartment and substance name, or by species number. For example, in our model the $c_{\text{H}_2\text{O in GAS}}$, or c_4 , is -36.6 in terms of the particular measure and scale used for the model.

2.5. Independent and Dependent Variables

Computation of a partial derivative involves an independent and a dependent variable. The independent variable is the one that is changed. The dependent variable is the one to be predicted as a result of the change.

2.5.1. Independent Variables in the Jacobian Package. Five kinds of independent variables may be used in the Jacobian package. They are called b, a, c, k, and g.

A "b" kind of independent variable refers to the amount of input of a component b_i . The "b" kind is identified by the component name or number.

An "a" kind of independent variable refers to an $a_{i,j}$ entry in the mass balance matrix A. It is identified by a component, compartment, and substance name or by a component and species number.

A "c" kind of independent variable refers to a c value (free energy value) attached to a species. It is identified by a compartment and substance name or by a species number.

A "k" kind of independent variable is a conversion of a "c" kind,

where $k = e^c$.^{*} The k value is also attached to a species and identified by a compartment and substance name or by a species number.

The remaining independent variable, g , identified by a compartment and substance name, shows the effect of changing the b 's associated with the components of a given species. It is used only in the Jacobian package and only in the form of an independent variable for a partial derivative. By the use of this g variable it is possible to observe the alterations in the amount of various species (containing more than one component) as the amounts of its components are altered.

The kinds of independent variables are summarized in Table 1.

Table 1

KINDS OF INDEPENDENT VARIABLES

Kind Designation	Refers to--
b	component
a	A matrix entry
c	free energy value
k	e^c
g	components of a species in the model

2.5.2. Dependent Variables. The dependent variables are quantities in the solution of the model preceding the Jacobian computations. The solution of our sample soda pop model is given in Fig. 3, and the following definitions may be clarified by reference to this figure.

The basic dependent variables used are x , \bar{x} , \hat{x} , and pH . The x 's are the mole numbers of the species in the solution, called MOLES in

^{*}For the case of the partial derivative with respect to the k value of an entire compartment, $k = e^0$ or 1.

Fig. 3. The \bar{x} 's are the mole totals for the compartments, called X-BAR in Fig. 3. The \hat{x} 's are the mole fractions of the species, that is, $\hat{x} = x/\bar{x}$, called MFRAC in Fig. 3. The pH, a measure of acidity, is defined elsewhere in descriptions of the chemical equilibrium program. It is called PH in Fig. 3. (If there is no hydrogen ion in a compartment, there is no pH.)

Also available to the Jacobian package as dependent variables are the logarithmic versions of the x 's, \bar{x} 's, \hat{x} 's, and pH. Partial derivatives of these variables give the fractional rate of change with respect to a change in the independent variables.

The names of dependent variables and their meanings are summarized in Table 2.

Table 2

KINDS OF DEPENDENT VARIABLES

Designation	Meaning
x	mole number
\bar{x}	mole total of compartment
\hat{x}	mole fraction (x/\bar{x})
pH	measure of acidity
$\log x$	logarithmic mole number
$\log \bar{x}$	logarithmic mole total
$\log \hat{x}$	logarithmic mole fraction
$\log \text{pH}$	logarithmic pH

3. CONTROL CARDS AND DATA CARDS

The Jacobian package may be used either with control cards, or by calling the subroutine JABY in NZSC, which is the main program of the chemical equilibrium code. In both cases data cards must be input

to select the independent variables for the computations. In both cases, data cards may also be used to control the number of dependent variables selected for computation and printing.

The control cards (or the subroutine JABY calling variables) select the kind of dependent variables and cause the computation and printing of the partial derivatives for these variables. This section describes the data and control cards and the use of the package with control cards. JABY is discussed in Sec. 5.

3.1. Control Cards

Table 3 lists the control cards available to the user. With the exception of LISTJABY, they are used to select the dependent variables and cause the computation and printing of the partial derivatives. All entries are left-adjusted to column 1 of the card.

Table 3
CONTROL CARDS

Control Card	Selects as Dependent Variables
MOLEJABY	x , \bar{x} , and pH
FRACTIONJABY	\hat{x} and pH
TOTALMOLEJABY	\bar{x} and pH
LOGMOLEJABY	log x , log \bar{x} , and log pH
LOGFRACTIONJABY	log \hat{x} and log pH
LOGTOTALJABY	log \bar{x} and log pH
LISTJABY	precedes list of data cards, causes data cards to be read and tested by program

} for all unsuppressed compartments

Before going into the details of card formats, we shall show, in Table 4, an example of the setup of a typical problem. This table

illustrates the order in which the cards are input and the columns in which the information is punched.*

First in order is a control card LISTJABY that causes the data cards to be read and listed in the program. Following it are the data cards, with an END card as the last data card. Next come control cards that select the dependent variables and direct the computation and printing of the various partial derivatives.

3.2. Data Cards

The data cards are punched according to the following format. They must be preceded by the control card LISTJABY and followed by an END card. All entries are left-adjusted in the columns indicated. Kinds of independent variables allowed are b, a, c, k, and g. Legal compartment, substance, and component names are discussed in the following paragraphs.

<u>Cols. 1-12</u>	<u>Cols. 13-18</u>	<u>Cols. 19-24</u>	<u>Col. 25</u>	<u>Cols. 31-42</u>
Compartment name	Substance name	Component name	Kind	Multiplier or blank

The contents of the data cards will be printed out, and erroneously punched cards will be labelled "illegal" and not included in the computations. The maximum number of legal data cards allowed (excluding compartment printing status cards discussed later) is 25.

If more than 25 legal cards are input, the extra cards will be checked

* In the case of control cards, the program requires only the first six letters of the control word to be punched. However, since the control word is printed in its entirety in the output, the results are more readable if the entire word is punched on the card.

Table 4
A TYPICAL PROBLEM

	Control Card or Compartment, cols. 1-12	Substance, cols. 13-18	Component, cols. 19-24	Kind, col. 25	Multiplier, cols. 31-42
Control card directs reading of data cards	LISTJABY				
Data cards	LIQUID LIQUID GAS END	NA+ OH- H2O	H+ ALL	C C A / B	.500
Control cards select dependent variables and cause computation and printing	MOLEJABY FRACTIONJABY				

NOTE: Detailed descriptions of card formats are given in Sec. 3 of the text.

for legality and the contents printed, but they will not be used in the computations.

3.2.1. Special Features of the Data Cards. The following paragraphs discuss various special entries allowed on the data cards in addition to those mentioned already. They include the use of MANY, ALL, and BAR as names; multipliers; slash cards used for spacing; and printing suppression cards.

ALL and MANY: In place of a particular compartment, substance, and/or component name identifying an independent variable, the words ALL or MANY may be used as a compartment, substance, and/or component name.

The use of ALL as a name will result in the selection of all of the compartments, substances, and/or components of the particular kind as independent variables.

The use of MANY as a name will result in the selection as independent variables only those of the particular kind for which the independent variable does not have a degenerate value. For example, this means that for a "b" kind, the b_i must not be zero; for an "a" kind, the $a_{i,j}$ matrix entry must not be zero; for a "c" kind, the c_j must not be zero; and for a "k" kind, the k_j must not be 1 ($c_j \neq 0$). MANY is not allowed for a "g" type.

ALL and MANY must not appear on the same card.

BAR: The word BAR may be used as a substance name for a "c" or "k" kind of derivative. This causes the selection of the c or k of the compartment total (\bar{c} or \bar{k}) as an independent variable, where $\bar{c} = \sum c_j$ and \bar{k} is arbitrarily set equal to \bar{c} .

Multiplier: Space is allocated on the data cards for a multiplier. A floating point number may be entered here. The results of the Jacobian computation will then be multiplied by this number before printing. The multiplier might be used, for example, to scale certain answers to cubic centimeters of gas at standard conditions instead of moles. If no multiplier is entered on the data card, the program sets it to 1.

Slash card: A card with a slash (/) in column 25 may be used to control the printing format. It has a function in the data list similar to that of a ¶ sign in a manuscript--that is, to start a new cycle of printing. If no slash card is used, the columns of partial derivatives are printed without a break (nominally eight columns per page). By using the slash card one can cause the program to print a specific page with fewer columns of derivatives. A slash card might be used, for example, to separate the different kinds of derivatives onto separate pages if more than one kind has been included in a data list. The slash card should be inserted in the data list where one wants the separation to occur. A new cycle of printing will begin with the next card following the slash card.

Compartment printing suppression: In normal usage the partial derivatives for all dependent variables of the problem are printed, that is, all compartments and/or all species. Since this sometimes causes a lot of paper to be used when one is interested in only a few items, the user has the power to suppress the printing of partial derivatives related to a compartment by means of a data card. The

card must have a compartment name in columns 1-12 and an "S" in column 25. The user may also unsuppress computations related to a compartment previously suppressed in a similar manner, but with a "U" in column 25. ALL is an acceptable compartment name. It may sometimes be more convenient, in a problem with many compartments where only the results for one compartment are needed, first to suppress all compartments and then to unsuppress the desired one, instead of suppressing each unwanted one individually. If more than one "S" or "U" card is input for the same compartment, the last one read dominates.

Cautions about data cards: Care must be taken in punching data cards, since incorrect ones will be rejected.

A card for kind "a," with compartment, substance, and component reading ALL, ALL, ALL will lead to the use of a great deal of paper. The user should think twice about any ALL, ALL combination.

3.2.2. Data Card Formats. Only certain combinations of data card entries are acceptable to the program. Table 5 on page 16 lists the allowable entries for each kind of derivative. Additional examples of data cards are given in Sec. 5.

4. EXAMPLES OF DATA CARDS

As we have seen, the format of a data card depends on the kind of independent variable selected and the function of the card. There are eight kinds of data cards, called b, a, c, k, g, u, s, and /. Examples of each kind will be given separately, followed, in Sec. 5, by a sample problem using all types of cards. The examples are drawn from our soda pop model, and the names and numbers refer to those given in Fig. 1.

Table 5

DATA CARD FORMATS

Compartment, cols. 1-12	Substance, cols. 13-18	Component, cols. 19-24	Type, col. 25	Multiplier, cols. 31-42
blank	blank	name, ALL, or MANY	b	floating point number or blank
name, MANY, or ALL	name, MANY, or ALL	name, MANY, or ALL	a	floating point number or blank
name, MANY, or ALL	name, BAR, MANY, or ALL	blank	c	floating point number or blank
name, MANY, or ALL	name, BAR, MANY, or ALL	blank	k	floating point number or blank
name or ALL	name or ALL	blank	g	floating point number or blank
blank	blank	blank	/	blank
name or ALL	blank	blank	S	blank
name or ALL	blank	blank	U	blank

NOTE: The data cards must be followed by a card with END in columns 1-3.

4.1. Kind "b"

The "b" data cards must have a component name, ALL or MANY in columns 19-24, and a "B" in column 25. The columns for compartment and substance name must be left blank. A multiplier may or may not be entered in columns 31-42. Table 6 shows the format for "b" data cards, and an explanation of each card follows the table.*

4.2. Kinds "c" and "k"

The "c" and "k" data cards must have entries for compartment name and substance name. The columns for component name must be left blank, and there must be a "C" or a "K" in column 25. ALL and MANY are permissible compartment names; ALL, MANY, and BAR are permissible substance names. Table 7 shows the format for "c" and "k" data cards.

4.3. Kind "a"

The "a" kind of data card must have entries in the compartment, substance, and component fields and an "A" in column 25. As usual, a multiplier may or may not be entered. ALL and MANY are permissible as names in all three fields. Table 8 shows the format for "a" data cards.

4.4. Kind "g"

A data card for kind "g" must have a compartment name, a substance name, and a "G" in column 25. The component name space must be left

* In our discussion of the names of kinds of independent variables, we refer to them as lowercase letters, as is done in other discussions of the chemical equilibrium program. However, since only capital letters are available for keypunching, the transformation to capitals is made here on examples of data cards. Also, superscripts and subscripts are placed on the level where they would be punched.

Table 6

FORMAT FOR "b" DATA CARDS

Card	Compartment, cols. 1-12	Substance, cols. 13-18	Component, cols. 19-24	Kind, col. 25	Multiplier, cols. 31-42
1			CO2	B	760.0
2			CO2	B	
3			ALL	B	
4			MANY	B	

Card 1 selects b_{CO_2} (b_2) as an independent variable.

Card 2 selects b_{CO_2} (b_2) as an independent variable but instructs the program to multiply the resulting partial derivatives by the multiplier 760, to give the results in terms of millimeters of mercury partial pressure per atmosphere instead of moles.

Card 3 selects all b's as independent variables.

Card 4 selects all nonzero b's as independent variables.

Table 7

FORMAT FOR "c" AND "k" DATA CARDS

Card	Compartment, cols. 1-12	Substance, cols. 13-18	Component, cols. 19-24	Kind, col. 25	Multiplier, cols. 31-42
1	LIQUID	H2CO3		C	
2	GAS	BAR		C	
3	GAS	ALL		K	
4	LIQUID	MANY		K	
5	ALL	H2O		C	
6	ALL	ALL		C	

Card 1 selects $c_{H_2CO_3}$ in LIQUID (c_{15}) as an independent variable.

Card 2 selects the c_{BAR} (see definition in Sec. 3) of the GAS compartment, $\bar{c}_{in\text{ GAS}}$ as an independent variable.

Card 3 selects the k's of all species in the GAS compartment (k_1, k_2, k_3, k_4) as independent variables.

Card 4 selects all the k's in the LIQUID compartment that are not 1 ($c \neq 0$) as independent variables. These are $k_5, k_{12}, k_{13}, k_{14}, k_{15}, k_{16}$.

Card 5 selects c_{H_2O} in GAS and c_{H_2O} in LIQUID as independent variables (c_4 and c_{13}).

Card 6 selects all the c's as independent variables (c_1 through c_{17}).

Table 8

FORMAT FOR "a" DATA CARDS

Card	Compartment, cols. 1-12	Substance, cols. 13-18	Component, cols. 19-24	Kind, col. 25	Multiplier, cols. 31-42
1	LIQUID	H2O	OH-	A	
2	GAS	ALL	CL-	A	
3	LIQUID	N2	ALL	A	
4	ALL	H2O	OH-	A	
5	LIQUID	MANY	CO2	A	
6	MANY	CO2	MANY	A	
7	ALL	ALL	ALL	A	

Card 1 selects a_{OH^-} , H₂O in LIQUID ($a_{5,13}$) as an independent variable.

Card 2 selects the a's for all species in the GAS compartment and the component Cl⁻ ($a_{6,1}$, $a_{6,2}$, $a_{6,3}$, and $a_{6,4}$) as independent variables.

Card 3 selects the a's for all the components in the N₂ in LIQUID column ($a_{1,7}$, $a_{2,7}$, ..., $a_{9,7}$) as independent variables.

Card 4 selects a_{OH^-} , H₂O in GAS and a_{OH^-} , H₂O in LIQUID ($a_{5,4}$ and $a_{5,13}$) as independent variables.

Card 5 selects all nonzero a's with CO₂ as component, in the LIQUID compartment ($a_{2,6}$, $a_{2,14}$, $a_{2,15}$, and $a_{2,16}$) as independent variables.

Card 6 selects all nonzero a's with CO₂ as substance ($a_{2,2}$ and $a_{2,6}$) as independent variables.

Card 7 selects all 153 a's as independent variables.

blank. A multiplier may or may not be entered. Table 9 shows the format for "g" data cards.

4.5. Compartment Printing Status Cards (Kinds "s" and "u")

Kind "s" and kind "u" data cards affect the dependent variables. Only entire compartments may be skipped or suppressed in the printing, so an "s" or "u" card must have a compartment name (or ALL), and an "S" or a "U" in column 25. The remaining entries should be blank. Table 10 shows the format for "s" and "u" data cards.

4.6. Slash Cards ("/" kind)

Slash cards end a cycle of printing and start a new one. No identifying names are necessary. Column 25, however, should have an entry that is a "/" . Several data cards are included in Table 11 to add meaning.

5. A SAMPLE PROBLEM AND INTERPRETATION OF RESULTS

5.1. The Sample Problem

A sample problem for the soda pop model is set up in this section and the results of the Jacobian computations are shown. Then numerical examples are given showing how to interpret the results.

The sample problem uses two separate lists of data cards and mixes several kinds of dependent and independent variables. Table 12 shows the control and data cards for the problem.

Note that here we are getting two different sets of derivatives. For each group the data cards are preceded by a LISTJABY card and are followed by an END card. For the first group, we are interested in

Table 9

FORMAT FOR "g" DATA CARDS

Card	Compartment, cols. 1-12	Substance, cols. 13-18	Component, cols. 19-24	Kind, col. 25	Multiplier, cols. 31-42
1	LIQUID	CO3=		G	
2	GAS	ALL		G	
3	ALL	CO2		G	
4	ALL	ALL		G	

Card 1 selects the g for CO₃ in the LIQUID compartment (g₁₆) as an independent variable.

Card 2 selects all g's in the GAS compartment (g₁, g₂, g₃, g₄) as independent variables.

Card 3 selects g's for CO₂ in both compartments (g₂ and g₆) as independent variables.

Card 4 selects all g's (g₁, g₂, ..., g₁₇) as independent variables.

Table 10

FORMAT FOR "s" AND "u" DATA CARDS

Card	Compartment, cols. 1-12	Substance, cols. 13-18	Component, cols. 19-24	Kind, col. 25	Multiplier, cols. 31-42
1	ALL			S	
2	GAS			U	
3	GAS			S	

Card 1 instructs the program, when printing is called for, to suppress all compartments. If this were the only "s" or "u" card in the data card list, no printing would occur.

Card 2, following card 1, now instructs the program to print only the GAS compartment derivatives.

Card 3, following the first two cards, brings the compartment printing status back to that of card 1. No printing will occur.

Table 11

FORMAT FOR SLASH (/) CARDS

Card	Compartment, cols. 1-12	Substance, cols. 13-18	Component, cols. 19-24	Kind, col. 25	Multiplier, cols. 31-42
1	GAS	ALL		C	
2				/	
3			ALL	B	
4				/	
5	LIQUID	O2	CO2	A	

Card 1 selects all c's in GAS compartment as independent variables (c_1, c_2, c_3, c_4).

Card 2 starts new page of printing after the last of the four columns of c derivatives.

Card 3 selects all b's as independent variables.

Card 4 starts new page of printing after last b derivative. In our example, there are nine b's. The program will print a page of eight columns, and a second page of one column. Then it starts another page with the "a" derivative of card 5.

Card 5 selects a_{CO_2, O_2} in LIQUID, or $(a_{2,5})$, as an independent variable.

Table 12

CONTROL AND DATA CARDS FOR SAMPLE PROBLEM

Compartment, cols. 1-12	Substance, cols. 13-18	Component, cols. 19-24	Kind, col. 25	Multiplier, cols. 31-42
LISTJABY				
LIQUID	H2O		C	
LIQUID	NA+		G	
LIQUID	HCO3-	GLUCOS	G	
			B	
			/	
GAS			S	
LIQUID	CO3=	MANY	A	
LIQUID	H2O		K	
LIQUID	CO2		K	
END				
MOLEJABY				
LISTJABY				
		GLUCOS	B	
		NA+	B	
		H+	B	
		OH-	B	
		CO2	B	760.0
END				
MOLEJABY				
FRACTIONJABY				
LCGMOLEJABY				

the effect on the pH, and in the LIQUID compartment. Since there is no pH for the GAS compartment (no H^+ in the compartment), we suppress the printing of this compartment. We select mole numbers as dependent variables by using the control card MOLEJABY. A slash card is used for easier reading of the results.

For the second set of independent variables we select the mole numbers, the mole fractions, and the logarithmic mole numbers as dependent variables by using the control cards MOLEJABY, FRACTIONJABY, and LOGMOLEJABY.

While we have suppressed the GAS compartment for the first list, it will not be suppressed for the second list, since the control card LISTJABY unsuppresses all compartments before reading the cards.

Figures 4 and 5 show the output produced by the Jacobian package for the first list of data cards. The control card LISTJABY produces the list of Fig. 4. Notice that a mispunched card is labelled illegal. The control card MOLEJABY produces two cycles of partial derivatives, shown in Fig. 5.

Figure 6 shows the LISTJABY output for the second group of data cards. Figure 6 also shows the output from the MOLEJABY control card. The output from the FRACTIONJABY control card is in Fig. 7, and the output from the LOGMOLEJABY card is in Fig. 8.

The multipliers are printed with the output only when at least one of the independent variables in a cycle of printing has a multiplier that is not 1.0. In our example they are printed only for the computations for the second list, since no multipliers were input by the first list (and the multipliers are therefore all set to 1.0).

LISTJABY

COMPARTMENT	SUBSTANCE	COMPONENT	TYPE	MULTIPLIER
LIQUID	H2O		C	1.0000000E 00
LIQUID	NA+		G	1.0000000E 00
LIQUID	HCO3-		G	1.0000000E 00
		GLUCOS	B	1.0000000E 00
			/	-0.
GAS			S	-0.
LIQUID	CO3=	MANY	A	1.0000000E 00
LIQUID	H2O		K	1.0000000E 00
LIQUID	CO2		K	-0.
END				-0.

ILLEGAL DATA

Fig. 4—First list of independent variables for Jacobian computations for Soda Pop Test problems

MOLEJABY

SODA POP TEST PROBLEM

CYCLE 1 MOLE NUMBER PARTIAL DERIVATIVES WITH RESPECT TO FOLLOWING INDEPENDENT VARIABLES

JACOB TYPE COMPONENT SUBSTANCE COMPARTMENT	C=FE NUMBER H2O LIQUID	G=INPUTS NA+ LIQUID	G=INPUTS HCO3- LIQUID	B=INPUT GLUCOSE
LIQUID	-6.50000E 00	1.13843E 00	1.13778E 00	1.13843E 00
PH	-3.44535E-01	-1.87961E-03	1.46729E 01	-1.87961E-03
O2	-8.93736E-06	1.12591E-06	1.12361E-06	1.12591E-06
CO2	-2.63959E-04	3.32519E-05	3.38718E-05	3.32519E-05
N2	-7.83263E-05	9.86737E-06	9.84719E-06	9.86737E-06
H+	1.97578E-08	8.61743E-10	-1.01850E-06	8.61743E-10
OH-	3.83811E-08	-7.75970E-10	1.92103E-05	-7.75970E-10
CL-	8.70447E-10	-0.	-0.	0.
NA+	9.58307E-10	1.00000E 00	-0.	0.
K+	5.25095E-10	-0.	-0.	0.
H2O	-6.49968E 00	1.38386E-01	1.40945E-01	1.38386E-01
HCO3-	7.53709E-05	4.07036E-07	9.93637E-01	4.07036E-07
H2CO3	1.46904E-06	8.01429E-09	9.02217E-09	8.01429E-09
CO3=	-3.69724E-05	-2.01715E-07	3.15965E-03	-2.01715E-07
GLUCOS	2.17476E-10	-0.	-0.	1.00000E 00

SODA POP TEST PROBLEM

CYCLE 2 MOLE NUMBER PARTIAL DERIVATIVES WITH RESPECT TO FOLLOWING INDEPENDENT VARIABLES

JACOB TYPE COMPONENT SUBSTANCE COMPARTMENT	A=MATRIX COEF CO2 LIQUID	A=MATRIX COEF H+ LIQUID	A=MATRIX COEF OH- LIQUID	K=C EX H2O LIQUID
LIQUID	1.02477E-04	2.10045E-04	1.16492E-04	-8.31329E 17
PH	1.44434E-02	2.98086E-02	2.43902E-02	-4.40649E 16
O2	3.75719E-10	7.41365E-10	5.32377E-10	-1.14306E 12
CO2	-1.03675E-07	-1.99303E-07	-1.56157E-07	-3.37596E 13
N2	3.29278E-09	6.49726E-09	4.66571E-09	-1.00177E 13
H+	-1.00322E-09	-2.07047E-09	-1.69415E-09	2.52695E 09
OH-	1.89035E-08	3.90131E-08	3.19214E-08	4.90882E 09
CL-	9.14717E-15	1.84453E-14	1.58865E-14	1.11327E 08
NA+	1.00705E-14	2.03072E-14	1.74900E-14	1.22564E 08
K+	5.51801E-15	1.11271E-14	9.58347E-15	6.71580E 07
H2O	-3.85049E-04	-8.19672E-04	-6.83641E-04	-8.31288E 17
HCO3-	9.75302E-04	2.01316E-03	1.64741E-03	9.63970E 12
H2CO3	-1.66668E-10	-3.24052E-10	-2.53648E-10	1.87885E 11
CO3=	-4.87673E-04	-9.83248E-04	-8.47120E-04	-4.72864E 12
GLUCOS	2.28536E-15	4.60845E-15	3.96913E-15	2.78144E 07

Fig.5—Mole number Jacobian output for Soda Pop Test problem

SODA POP TEST PROBLEM

LISTJABY

COMPARTMENT	SUBSTANCE	COMPONENT	TYPE	MULTIPLIER
		GLUCOS	B	1.0000000E 00
		NA+	B	1.0000000E 00
		H+	B	1.0000000E 00
		OH-	B	1.0000000E 00
		CO2	B	7.6000000E 02
END				-0.

MOLEJABY

SODA POP TEST PROBLEM

CYCLE 1 MOLE NUMBER PARTIAL DERIVATIVES WITH RESPECT TO FOLLOWING INDEPENDENT VARIABLES

JACOB TYPE COMPONENT MULTIPLIER	B=INPUT GLUCOSE 1.00000E 00	B=INPUT NA+ 1.00000E 00	B=INPUT H+ 1.00000E 00	B=INPUT OH- 1.00000E 00	B=INPUT CO2 7.60000E 02
GAS	-1.38430E-01	-1.38430E-01	1.20007E 00	-1.19933E 00	8.09209E 02
O2	-1.12595E-06	-1.12595E-06	7.17365E-07	-1.65215E-06	4.01430E-04
CO2	-3.34652E-05	-3.34652E-05	9.96596E-01	-9.96624E-01	7.59843E 02
N2	-9.86834E-06	-9.86834E-06	6.28728E-06	-1.44684E-05	3.51434E-03
H2O	-1.38386E-01	-1.38386E-01	2.03466E-01	-2.02683E-01	4.93627E 01
LIQUID	1.13843E 00	1.13843E 00	-2.03285E-01	1.20254E 00	-4.92153E 01
PH	-1.87961E-03	-1.87961E-03	-1.47486E 01	1.47393E 01	-5.04748E 01
O2	1.12591E-06	1.12591E-06	-7.17514E-07	1.65205E-06	-4.01621E-04
CO2	3.32519E-05	3.32519E-05	1.92892E-04	-1.65292E-04	1.51365E-01
N2	9.86737E-06	9.86737E-06	-6.28824E-06	1.44785E-05	-3.51977E-03
H+	8.61743E-10	8.61743E-10	1.02435E-06	-1.02307E-06	3.47454E-06
OH-	-7.75970E-10	-7.75970E-10	-1.92980E-05	1.92980E-05	-6.66786E-05
CL-	0.	0.	0.	0.	0.
NA+	0.	1.00000E 00	0.	0.	0.
K+	0.	0.	0.	0.	0.
H2O	1.38386E-01	1.38386E-01	7.93307E-01	2.05904E-01	-4.93686E 01
HCO3-	4.07036E-07	4.07036E-07	-9.93621E-01	9.93623E-01	1.09827E-02
H2CO3	8.01429E-09	8.01429E-09	3.13629E-07	-2.74160E-07	2.15218E-04
CO3=	-2.01715E-07	-2.01715E-07	-3.16777E-03	3.16677E-03	-5.41675E-03
GLUCOS	1.00000E 00	0.	0.	0.	0.

Fig.6—Second list independent variables for Jacobian computations and mole number Jacobian output for Soda Pop Test problem

FRACTIONJABY

SODA POP TEST PROBLEM

CYCLE 1 MOLE FRACTION PARTIAL DERIVATIVES WITH RESPECT TO FOLLOWING INDEPENDENT VARIABLES

JACOB TYPE	B=INPUT	B=INPUT	B=INPUT	B=INPUT	B=INPUT
COMPONENT	GLUCOSE	NA+	H+	OH-	CO2
MULTIPLIER	1.00000E 00	1.00000E 00	1.00000E 00	1.00000E 00	7.60000E 02
GAS					
O2	7.30128E-05	7.30128E-05	-6.33049E-04	6.32646E-04	-4.26866E-01
CO2	8.33050E-05	8.33050E-05	9.24027E-03	-9.24101E-03	7.10905E 00
N2	1.14292E-03	1.14292E-03	-9.90895E-03	9.90269E-03	-6.68161E 00
H2O	-1.29924E-03	-1.29924E-03	1.30169E-03	-1.29431E-03	-5.67187E-04
LIQUID					
PH	-1.87961E-03	-1.87961E-03	-1.47486E 01	1.47393E 01	-5.04748E 01
O2	1.29484E-09	1.29484E-09	-1.12258E-08	1.12196E-08	-7.57025E-06
CO2	3.81019E-08	3.81019E-08	4.22630E-06	-4.22663E-06	3.25152E-03
N2	1.13486E-08	1.13486E-08	-9.83909E-08	9.83288E-08	-6.63451E-05
H+	2.77972E-12	2.77972E-12	2.18113E-08	-2.17976E-08	7.46462E-08
OH-	-3.09897E-10	-3.09897E-10	-4.10803E-07	4.10547E-07	-1.40691E-06
CL-	-4.13069E-05	-4.13069E-05	7.37603E-06	-4.36330E-05	1.78573E-03
NA+	-4.54763E-05	2.12446E-02	8.12054E-06	-4.80371E-05	1.96598E-03
K+	-2.49183E-05	-2.49183E-05	4.44957E-06	-2.63215E-05	1.07724E-03
H2O	-2.11529E-02	-2.11529E-02	2.11929E-02	-2.10725E-02	-9.23399E-03
HC03-	-1.51652E-05	-1.51652E-05	-2.11516E-02	2.11383E-02	8.89800E-04
H2CO3	-7.81855E-10	-7.81855E-10	6.84727E-09	-6.84300E-09	4.62319E-06
CO3=	-2.84218E-08	-2.84218E-08	-6.74378E-05	6.73954E-05	-1.14280E-04
GLUCOS	2.12798E-02	-1.03203E-05	1.84285E-06	-1.09014E-05	4.46154E-04

Fig. 7—Mole fraction Jacobian output for Soda Pop Test problem

LOGMOLEJABY

SODA POP TEST PROBLEM

CYCLE 1 MOLE NUMBER LOGARITHMIC DERIVATIVES (FRACTIONAL RATE OF CHANGE) WITH RESPECT TO FOLLOWING INDEPENDENT VARIABLES

JACOB TYPE COMPONENT MULTIPLIER	B=INPUT GLUCOSE 1.00000E 00	B=INPUT NA+ 1.00000E 00	B=INPUT H+ 1.00000E 00	B=INPUT OH- 1.00000E 00	B=INPUT CO2 7.60000E 02
GAS	-1.38422E-03	-1.38422E-03	1.20000E-02	-1.19925E-02	8.09161E 00
O2	-2.13418E-07	-2.13418E-07	1.35973E-07	-3.13157E-07	7.60891E-05
CO2	-5.53808E-06	-5.53808E-06	1.64925E-01	-1.64929E-01	1.25745E 02
N2	-1.19500E-07	-1.19500E-07	7.61356E-08	-1.75205E-07	4.25556E-05
H2O	-2.26584E-02	-2.26584E-02	3.33142E-02	-3.31860E-02	8.08232E 00
LIQUID	2.42373E-02	2.42373E-02	-4.32796E-03	2.56021E-02	-1.04780E 00
PH	-2.52369E-04	-2.52369E-04	-1.98023E 00	1.97899E 00	-6.77707E 00
O2	2.56213E-02	2.56213E-02	-1.63278E-02	3.75943E-02	-9.13933E 00
CO2	2.56160E-02	2.56160E-02	1.48597E-01	-1.27335E-01	1.16605E 02
N2	2.56214E-02	2.56214E-02	-1.63279E-02	3.75945E-02	-9.13936E 00
H+	2.85652E-02	2.85652E-02	3.39555E 01	-3.39129E 01	1.15175E 02
OH-	-1.36484E-03	-1.36484E-03	-3.39428E 01	3.39429E 01	-1.17280E 02
CL-	0.	0.	0.	0.	0.
NA+	0.	1.13469E 01	0.	0.	0.
K+	0.	0.	0.	0.	0.
H2O	2.96313E-03	2.96313E-03	1.69864E-02	4.40884E-03	-1.05708E 00
HCO3-	1.38420E-05	1.38420E-05	-3.37899E 01	3.37900E 01	3.73486E-01
H2CO3	4.34181E-03	4.34181E-03	1.69911E-01	-1.48528E-01	1.16596E 02
CO3=	-4.31412E-03	-4.31412E-03	-6.77497E 01	6.77284E 01	-1.15849E 02
GLUCOS	5.00000E 01	0.	0.	0.	0.

Fig. 8—Logarithmic mole number output for Soda Pop Test problem

The multiplier of 760.0 for the b_{CO_2} data card was computed to convert the mole fraction of CO_2 in the GAS compartment to millimeters of partial pressure. The results are therefore meaningful only for the mole fraction computations for the GAS compartment (see Fig. 7).

5.2. Numerical Examples of Interpretation of Results

The data for these examples is taken from the preceding tables for our sample problem.

Example 1: Predicting the effect on compartment size (mole totals) of increasing the amount of glucose input.

For this example we use the partial derivatives of b_g (glucose) for the dependent variables \bar{x}_{GAS} and \bar{x}_{LIQUID} . The \bar{x} 's from the solution (see Fig. 3) are in column 1 below. The b Jacobians (from Fig. 6) are in column 2. They show the number of moles of change in each compartment when 1 mole of glucose is added. Column 3, the sum of columns 1 and 2, shows the predicted size of the compartments after the addition of glucose. Columns 4 and 5 show the predicted size of the compartments as a result of adding 10 and 100 moles of glucose, obtained by multiplying column 2 by 10 and 100, respectively, and adding to column 1.

Total Moles (\bar{x}) (dependent variable)	Partial Derivative $b_{GLUCOSE}$	Resulting Compartment Moles When Adding Glucose--		
		1 Mole	10 Moles	100 Moles
GAS 100.006	-0.138430	99.86757	98.6217	86.163
LIQUID 46.9702	1.13843	48.10863	58.3545	160.8132

As larger amounts of glucose are added, the size (in moles) of the GAS compartment decreases, and the size of the LIQUID compartment

increases. Eventually the number of moles in the LIQUID compartment becomes larger. As an exercise, we now predict how many moles of glucose must be added to make the compartments have an equal number of moles. We set up the equation

$$\begin{array}{lcl} 100.006 \text{ moles} - .13843y & = & 46.9702 \text{ moles} + 1.13843y \\ (\text{GAS } \bar{x}) & & (\text{LIQUID } \bar{x}) \end{array}$$

and solve for y, which turns out to be 41.536 moles. Inserting y in the above equation we have

$$\begin{aligned} & 100.006 \text{ moles} - (.13843 \times 41.536 \text{ moles}) \\ & = 46.9702 \text{ moles} + (1.13843 \times 41.536 \text{ moles}) , \end{aligned}$$

or

$$94.256 \text{ moles} = 94.256 \text{ moles}.$$

The compartments are predicted to be equal in size, each having 94.256 moles, when 41.536 moles of glucose are added.

Example 2: Predicting the effect on pH when the free energy values of H_2O in the LIQUID compartment is changed.

For this example we use the partial derivatives of pH for c_{13} ($c_{\text{H}_2\text{O}}$ in LIQUID). The pH of the problem is from the solution in Fig. 3. The partial derivative is from Fig. 5. Since the partial

Dependent Variable	Partial Derivative	pH After Adding	pH After Subtracting
pH LIQUID	$c_{\text{H}_2\text{O}}$ in LIQUID	1 unit to c_{13}	1 unit from c_{13}
7.44788	-0.344535	7.103345	7.792415

derivative for c_{13} is negative, an increase in c_{13} decreases the pH, and a decrease in c_{13} increases the pH.

Now we shall do an exercise similar to that in the first example. We shall predict the amount of change necessary in this c value to bring the pH down to 6.5. We set up the following equation and solve for y :

$$\begin{array}{rcl} 7.44788 & - & .344535y \\ \text{(original pH)} & \text{(} c_{13} \text{ derivative)} & = 6.5 \end{array}$$

Here $y = 2.75118$ units; that is, the c_{H_2O} in LIQUID must be increased by that many units to achieve a pH of 6.5.

Example 3: Predicting the effect on H_2O and pH from an addition of an NaOH solution.

In practical applications one seldom changes species or components singly. An example is given of a change in several components where a tenth of a mole of NaOH and a liter of water are added. See Table 13. To predict the effect of this addition on the number of moles in H_2O in GAS, in H_2O in LIQUID, and in pH of the LIQUID compartment, we sum the increments obtained from the derivatives of these species with respect to b_{Na^+} , b_{OH^-} , and b_{H^+} . Since H_2O is not present in our model as a component, we add H^+ and OH^- in equal proportions to provide the H_2O addition. The partial derivatives are in terms of one mole change, so the NaOH derivatives must be multiplied by 0.1 and the water derivatives by 55.14 (moles of H_2O per liter). The partial derivatives are from Fig. 6.

The same predictions can be made using the logarithmic derivatives of Fig. 8, instead of the mole number derivatives. The logarithmic

Table 13

EXAMPLE OF EFFECT OF ADDING AN NaOH SOLUTION

Dependent Variable	Mole Number Derivatives	Proportion of Derivatives
H ₂ O in GAS	Na ⁺ -0.138386	0.1 (Na ⁺) = -0.0138386
	OH ⁻ -0.0202683	0.1 (OH ⁻) = -0.0202683
	H ⁺ 0.203466	55.14(H ⁺) = 11.2191
		55.14(OH ⁻) = -11.1759
		0.0091 moles increase in H ₂ O in GAS predicted
H ₂ O in LIQUID	Na ⁺ 0.138386	0.1 (Na ⁺) = 0.013839
	OH ⁻ 0.205904	0.1 (OH ⁻) = 0.020590
	H ⁺ 0.793307	55.14(H ⁺) = 43.7429
		55.14(OH ⁻) = 11.3535
		55.1308 moles increase in H ₂ O in LIQUID predicted
pH in LIQUID	Na ⁺ -0.0018796	0.1 (Na ⁺) = -0.0001879
	OH ⁻ 14.7393	0.1 (OH ⁻) = 1.47393
	H ⁺ -14.7486	55.14(H ⁺) = -813.2378
		55.14(OH ⁻) = 812.7250
		0.96095 increase in pH predicted

derivatives show the percentage change as a result of the infusion.

The computations for the pH example are shown below:

log x derivative of pH in LIQUID for--	$\text{Na}^+ \quad -0.0002524$ $\text{OH}^- \quad \underline{1.97899}$ 1.97874	$0.1(\text{NaOH}) = 0.197874$
	$\text{H}^+ \quad -1.98023$ $\text{OH}^- \quad \underline{1.97899}$ $\text{H}_2\text{O} \quad -0.00124$	$55.14(\text{H}_2\text{O}) = \underline{-0.068373}$ 0.129501

<u>Original pH</u>	<u>Increase</u>	
7.44788	x	$0.129501 = 0.9645 \text{ increase in pH}$

By summing the logarithmic derivatives we see that the addition of this infusion should cause an increase of about 12.95 percent in the pH, or an increase of 0.9645, which agrees fairly closely with our mole number derivative prediction.

Example 4: Predicting the effect on H_2O in the LIQUID compartment from the addition of a mole of NaHCO_3 . For this computation we add the g derivatives of the species Na^+ and HCO_3^- in LIQUID. The derivatives are from Fig. 5.*

*The components of HCO_3^- in our model are CO_2 and OH^- (see Fig. 1). The g derivative combines the effect of these components in the ratio given by the detached coefficients. Na^+ as a species in our model has only one component, Na^+ , with a detached coefficient of 1. Therefore the g derivative for Na^+ is the same as the b derivative for Na^+ (see the Jacobian formulas in Appendix B).

\bar{x}_{H_2O} in LIQUID	46.7026	moles	(from Fig. 3)
g derivative for Na^+	0.138386		
g derivative for HCO_3^-	$\frac{0.140945}{46.981931}$	=	predicted number of moles of H_2O

Example 5. Predicting the effect on the concentration of water in the LIQUID compartment of adding a mole of glucose.

The dependent variable here is \hat{x}_{H_2O} in LIQUID, the concentration of H_2O in LIQUID, and is taken from Fig. 3. The \hat{x} partial derivative for $b_{GLUCOSE}$ is taken from Fig. 7. The prediction is obtained, as before, by adding the partial derivative to the original value.

Dependent Variable	\hat{x} Partial Derivative	Predicted Concentration
\hat{x}_{H_2O} in LIQUID 0.994302	$b_{GLUCOSE}$ -0.0211529	0.9731491

Thus the concentration of H_2O in LIQUID should decrease from 99.43 percent to 97.31 percent when a mole of glucose is added.

The same prediction could be achieved by using the mole number derivatives (Fig. 6) in the slightly more tedious computation shown below:

Item	Solution Values	$b_{GLUCOSE}$ Mole Number Derivatives	Predicted Result of Adding One Mole
\bar{x}_{H_2O} in LIQUID	46.7026	0.138386	46.84099
\bar{x} in LIQUID	46.9702	1.13843	48.1086
Concentration (\bar{x}/\bar{x})	0.9943		0.9736

While the amount of water in the LIQUID compartment increases when a mole of glucose is added, the concentration of water decreases.

6. DETAILED DESCRIPTION OF JABY PACKAGE FOR NZSC USERS

The remainder of this study describes in detail the subroutines for the user who may wish to call them directly through the NZSC routine.

The package consists of five programs:

Subroutine JABY (KDEP)

Subroutine LIST

Function PART (KDEP, JNUM, KIND, NCOL, NROW)

Function BJACOB (JNUM, NROW)

Function CJACOB (JNUM, NCOL)

Partial derivatives may be obtained by using JABY, the control routine, or by directly calling the others.

6.1. Subroutine JABY

JABY controls the reading of the data cards, and the computation and printing of partial derivatives. Calling JABY (KDEP) in NZSC is equivalent to using the control cards previously described, as follows:

<u>NZSC</u>	<u>Control card</u>	<u>Function</u>
CALL JABY(0)	LISTJABY	Reads and lists data cards

Selects as dependent variables:

CALL JABY(1)	MOLEJABY	x , \bar{x} , and pH
CALL JABY(2)	FRACTIONJABY	\hat{x} and pH

<u>NZSC</u>	<u>Control Card</u>	<u>Function</u>
		Selects as dependent variables:
CALL JABY(3)	TOTALMOLEJABY	\bar{x} and pH
CALL JABY(4)	LOGMOLEJABY	$\log x$, $\log \bar{x}$, and $\log pH$
CALL JABY(5)	LOGFRACTIONJABY	$\log \hat{x}$ and $\log pH$
CALL JABY(6)	LOGTOTALMOLEJABY	$\log \bar{x}$ and $\log pH$

Data cards must be input as described in Sec. 3. The user must call JABY(0) to read the data cards, and then select the dependent variable by one of the other JABY calls. Data cards must always be followed by an END card.

6.2. Subroutine LIST

Subroutine LIST reads the data cards for the Jacobian computation and from them forms two lists: a list of selected independent variables (LS) and a list of compartment printing status (LC). The program checks the LS data cards and rejects those that are incorrectly filled out. The contents of the cards are printed, with illegal cards identified as such. The maximum length of the list of selected variables, called LLS, is 25. If more than 25 legal cards (excluding the compartment printing status cards) are input, LIST will process and print the contents of the excess cards but not include them in the computations.

6.2.1. Compartment Printing Status List. This list is kept separately by the program. There is always an entry for each compartment, and when LIST is called, all compartments are put in an unsuppressed state. They remain so until a data card is read in to change that state.

6.2.2. Direct Access to the Independent Variable List. This list

has dimensions (25,4). The information stored in the list by the program is in terms of compartment, species, component, and type numbers, and multipliers. It is possible to add to or change items on the list in NZSC by putting these numbers in the correct list entries. Responsibility for the correctness of such additions or changes lies with the user, for all checks for validity are in the LIST routine that he is bypassing. If a list is being added to, the value of LLS must be increased; the length of the list may be decreased by reducing LLS.

The following are permissible entries for the list, LS(25,4):

Item Name	Contents				
	LS(I,1)	LS(I,2)	LS(I,3)	LS(I,4)	XMULT(I)
contents	compartment number	species number	component number	KIND number	multiplier
	or	or	or	=	Floating point number
	-1 for ALL	-1 ALL	-1 ALL	1 for /	
	-2 for MANY	-2 MANY	-2 MANY	2 " b	
		-3 BAR		3 " a	
				4 " c	
				5 " k	
				6 " g	

Care should be taken to include a multiplier in XMULT(I) for each entry, for this will not be set to 1.0 when changing the list directly.

6.2.3. Direct Access to Compartment Printing Status List. This list, called LC, has a dimension of (25). It allows one entry for each of the compartments (up to 25) in the chemical equilibrium program. An entry may be changed directly by an NZSC card setting LC(k) to 0 or 1, where k is the compartment number, 0 means unsuppress, and 1 means

suppress. The block of common storage labelled COMMON/JAC/ must be added to the NZSC routine for any direct change in LS or LC entries.

6.3. Function PART (KDEP, JNUM, KIND, NCOL, NROW)

The function PART computes the partial derivatives (using the functions BJACOB and CJACOB). It is normally called by JABY but may be directly called through NZSC.

PART will compute $\frac{\partial u}{\partial v}$ where, if

KDEP = 1,	$u = x_{JNUM}$,
KDEP = 2,	$u = \hat{x}_{JNUM}$,
KDEP = 3,	$u = \bar{x}_{JNUM}$,
KDEP = 4,	$u = \log x_{JNUM}$,
KDEP = 5,	$u = \log \hat{x}_{JNUM}$,
KDEP = 6,	$u = \log \bar{x}_{JNUM}$,
KDEP = -1,	$u = pH_{JNUM}$,
KDEP = -2,	$u = \log pH_{JNUM}$,

and JNUM is always the species number of the dependent variable (for a compartment, JNUM is the negative of the compartment number); and if

KIND = 2,	$v = b_{NROW}$,	and NCOL is 0,
KIND = 3,	$v = a_{NROW, NCOL}$,	
KIND = 4,	$v = c_{NCOL}$,	and NROW is 0,
KIND = 5,	$v = k_{NCOL}$,	and NROW is 0,
KIND = 6,	$v = g_{NCOL}$,	and NROW is 0.

NROW is always the component number. NCOL is the species number, with the compartment NCOL set to the negative of the compartment number.

When the derivative of the pH is wanted, JNUM should be set to either the species number of H^+ in the selected compartment, or the negative of the compartment number.

ARITH must be called before any use of PART directly. After ARITH is called, PART may be used any number of times until the information computed by ARITH is destroyed. Observe that most of the system routines will destroy this information, but PART will not.

No printing occurs, except for error messages.

6.4. Functions BJACOB (JNUM, NROW) and CJACOB (JNUM, NCOL)

The function BJACOB computes the partial derivative

$$\frac{\partial u}{\partial v}, \quad \text{where } v \text{ is } b_{NROW} \text{ and } u \text{ is } x_{JNUM}.$$

The function CJACOB computes the partial derivative

$$\frac{\partial u}{\partial v}, \quad \text{where } v \text{ is } c_{NCOL} \text{ and } u \text{ is } x_{JNUM}.$$

For a compartment derivative, JNUM is set to the negative of the compartment number, for both functions. No printing occurs for either function.

CJACOB was a part of the previous Jacobian package and has not been changed.

Appendix A

QUICK REFERENCE GUIDE

This Appendix is a quick reference guide for users of the package. It summarizes in tabular form the control card and data information and the calling variables for the various subroutines.

1. Control Cards

<u>Control Card</u>	<u>NZSC Equivalent</u>	<u>Function</u>
LISTJABY	CALL JABY(0)	Read data cards
MOLEJABY	CALL JABY(1)	Print x , \bar{x} , pH derivatives
FRACTIONJABY	CALL JABY(2)	Print \hat{x} , pH derivatives
TOTALMOLEJABY	CALL JABY(3)	Print \bar{x} , pH derivatives
LOGMOLEJABY	CALL JABY(4)	Print $\log x$, $\log \bar{x}$, pH derivatives
LOGFRACTIONJABY	CALL JABY(5)	Print \hat{x} , \log pH derivatives
LOGTOTALMOLEJABY	CALL JABY(6)	Print $\log x$, \log pH derivatives

2. Data Card Format

Data cards must have a name or blank in the columns indicated.

Allowable names are defined below.

Compartment, cols. 1-12	Substance, cols. 13-18	Component, cols. 19-24	Kind, col. 25	Multiplier, cols. 31-42
		name	b	floating point
name	name	name	a	number
name	name		c	or
name	name		k	blank
name	name		g	
name			s	blank
name			u	blank

Allowable names are:

Compartment, substance, or component names (in proper columns)
for all kinds.

ALL for all kinds.

MANY for "a," "c," and "k" kinds.

BAR for "c" and "k" kinds substance name.

3. Calling Variables for PART (KDEP, JNUM, KIND, NCOL, NROW)

Number	for KDEP means	for KIND means	JNUM: number of dependent species or negative of dependent compart- ment
1	x	nothing	
2	\hat{x}	b	
3	\bar{x}	a	NCOL: number of independent species or negative of independent com- partment
4	log x	c	
5	log \hat{x}	k	
6	log \bar{x}	g	
7	pH	nothing	
8	log pH	nothing	NROW: number of independent component

4. LIST Items

LS(I,1) = compartment number;
 LS(I,2) = species number (not substance);
 LS(I,3) = component number;
 LS(I,4) = kind number, where 1 = /,
 2 = b,
 3 = a,
 4 = c,
 5 = k,
 6 = g;

XMULT(I) = floating point multiplier.

ALL, MANY, and BAR may be put on the list in accordance with the restrictions on the data cards (see "Data Card Format," Sec. 2 of this Appendix). The numbers for these are

-1 for ALL,
 -2 for MANY,
 -3 for BAR.

5. BJACOB (JNUM, NROW)

JNUM is dependent species number or negative of dependent compartment number.

NROW is independent component number.

6. CJACOB (JNUM, NCOL)

JNUM is dependent species number or negative of dependent compartment number.

NCOL is independent species number or negative of independent compartment number.

Appendix B

JACOBIAN FORMULAS

N	=	number of species
M	=	number of components
K	=	number of compartments
a	=	the augmented $(M + K)$ by $(N + K)$ mass balance matrix
k, i	=	indices varying over components and compartments
z, j	=	indices varying over species and compartments
c_j	$\left\{ \begin{array}{l} = \\ = \end{array} \right.$	$\left\{ \begin{array}{l} \text{if } j \text{ is a species, the Gibbs parameter for that species} \\ \text{if } j \text{ is a compartment, the Gibbs parameter for that compartment (always zero in the existing program)} \end{array} \right.$
b_i	$\left\{ \begin{array}{l} = \\ = \end{array} \right.$	$\left\{ \begin{array}{l} \text{if } i \text{ is a component, the input for that component} \\ \text{if } i \text{ is a compartment, zero} \end{array} \right.$
d_j	$\left\{ \begin{array}{l} = \\ = \end{array} \right.$	$\left\{ \begin{array}{l} \text{if } j \text{ is a species, } 1 \\ \text{if } j \text{ is a compartment, } -1 \end{array} \right.$
x_j	=	if j is a species, the number of moles of j
\bar{x}_j	=	if j is a compartment, the total number of moles in j
π_i	=	the Lagrangian multiplier associated with i (relative to the augmented matrix)
δ	=	the Kronecker delta
pH	=	$-\log (ALITER \text{ BLITER } \hat{x}_H+)/\log (10)$
\log	=	the Napierian logarithm when written without a subscript
u	=	any dependent variable
v	=	any independent variable
$\langle j \rangle$	$\left\{ \begin{array}{l} = \\ = \end{array} \right.$	$\left\{ \begin{array}{l} \text{if } j \text{ is a species, the compartment in which } j \text{ occurs} \\ \text{if } j \text{ is a compartment, undefined} \end{array} \right.$

$$\begin{aligned} \hat{x}_j & \begin{cases} = & \text{if } j \text{ is a species, } x_j / \bar{x}_{<j>} \\ = & \text{if } j \text{ is a compartment, undefined} \end{cases} \\ k_j & = e^{c_j} \end{aligned}$$

$$(1) \quad r_{k,i} = \sum_j a_{kj} a_{ij} d_j x_j$$

$$(2) \quad \frac{\partial x_j}{\partial b_i} = d_j x_j \sum_k a_{kj} r_{ki}^{-1}$$

$$(3) \quad \frac{\partial x_\ell}{\partial c_j} = -d_j x_j \delta_\ell^j + d_\ell d_j x_\ell x_j \sum_{i,k} a_{i\ell} a_{kj} r_{ik}^{-1}$$

$$(4) \quad \frac{\partial \hat{x}_j}{\partial v} = \left(\frac{\partial x_j}{\partial v} - \hat{x}_j \frac{\partial \bar{x}_{<j>}}{\partial v} \right) / \bar{x}_{<j>}$$

$$(5) \quad \frac{\partial \text{pH}}{\partial v} = \frac{-\partial \hat{x}_{H^+}}{\partial v} / (\hat{x}_{H^+} \log 10)$$

$$(6) \quad \frac{\partial \log u}{\partial v} = \frac{\partial u}{\partial v} / u$$

$$(7) \quad \frac{\partial u}{\partial k_j} = e^{-c_j} \frac{\partial u}{\partial b_i}$$

$$(8) \quad \frac{\partial u}{\partial a_{ij}} = -\pi_i \frac{\partial u}{\partial c_j} - x_j \frac{\partial u}{\partial b_i}$$

$$(9) \quad \frac{\partial u}{\partial g_j} = \sum_i a_{ij} \frac{\partial u}{\partial b_i}$$

BIBLIOGRAPHY

- Clasen, R. J., The Numerical Solution of the Chemical Equilibrium Problem, The RAND Corporation, RM-4345, January 1965.
- Dantzig, G. B., J. H. Folkman, and N. Z. Shapiro, "On the Continuity of the Minimum Set of a Continuous Function," J. Math. Anal. & Appl., Vol. 17, No. 3, March 1967.
- Dantzig, G. B., and J. C. DeHaven, "On the Reduction of Certain Multiplicative Chemical Equilibrium Systems to Mathematically Equivalent Additive Systems," Journal of Chem. Phys., Vol. 36, No. 10, 1962, pp. 2620-2627.
- Dantzig, G. B., C. F. Sams, J. C. DeHaven, I. Cooper, S. M. Johnson, E. C. DeLand, and H. E. Kanter, "A Mathematical Model of the Human External Respiratory System," Perspective in Biology & Medicine, Vol. 4, No. 3, 1961, p. 324.
- DeHaven, J. C., and N. Z. Shapiro, "On the Control of Urine Formation," Supplementum Ad Nephron, Vol. 4, 1967.
- DeHaven, J. C., E. C. DeLand, N. S. Assali, and W. Manson, Physiocochemical Characteristics of Placental Transfer, The RAND Corporation, P-2565-1, February 1965.
- DeHaven, J. C., and E. C. DeLand, The Reactions of Hemoglobin and Steady States in the Human Respiratory System: An Investigation Using Mathematical Models and an Electronic Computer, The RAND Corporation, RM-3212-PR, December 1962.
- Shapiro, N. Z., and L. S. Shapley, On Membrane Equilibria, The RAND Corporation, RM-4464-PR, July 1966.
- Shapiro, N. Z., and L. S. Shapley, "Mass Action Laws and the Gibbs Free Energy Function," J. Soc. Indust. App. Math., Vol. 13, No. 2, June 1965.
- Shapiro, N. Z., A Generalized Technique for Eliminating Species in Complex Chemical Equilibrium Calculations, The RAND Corporation, RM-4205-PR, September 1964.
- Shapiro, N. Z., On the Behavior of a Chemical Equilibrium System When Its Free Energy Parameters are Changed, The RAND Corporation, RM-4128-PR, May 1964.
- Shapiro, N. Z., Conditions for a Homogeneous Mixture to be Ideal, The RAND Corporation, RM-3677-PR, June 1963.