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A PROGRAM FOR THE STATISTICAL ANALYSIS OF DEFECTS IN NONSTOICHIOMETRIC METAL OXIDES

by

A. J. Strecok and L. M. Atlas

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June 1968

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I. INTRODUCTION

In a nonstoichiometric metal oxide the point defects (e.g., vacancies, interstitial ions, and localized electrons or localized holes) are generally not arranged in a perfectly uniform pattern. At any instant, therefore, the local mean spacing between defects and the resultant energy of a single defect vary with position. Averaged over a period of time, the defects in an equilibrium assembly have a characteristic distribution over the possible range of spacings and energies. The form of this distribution may be determined approximately with a statistical system that divides the spacing and energy ranges into discrete levels by means of a control integer (the spacing parameter). The required computations and the estimation of certain thermodynamic quantities from the results are governed by a program described in the succeeding sections.

Let a crystal that contains an assembly of like defects be divided at any instant into small cells, each containing one defect. In a given cell, the maximum number of lattice points that can simultaneously accommodate defects is the spacing parameter. This number is a measure of the cell volume and therefore of the local mean defect spacing. A set of spacing subclasses may be established by assigning to the spacing parameter a set of integer values: C, C-1, ..., C-i, ..., C-L. Each integer generates a corresponding level of energy: $\epsilon_0, \epsilon_1, \ldots, \epsilon_i, \ldots, \epsilon_L$, and each level contains a fraction $y_0, y_1, \ldots, y_i, \ldots, y_L$ of the total number of defects.

In ionic crystals two assemblies of defects commonly coexist in mutual compensation. If a compound is hypostoichiometric, anion vacancies (or interstitial cations) may occur together with cations of *lower* than normal positive charge. If it is hyperstoichiometric, cation vacancies (or interstitial anions) may coexist with cations of *higher* than normal positive charge. Subscript A hereafter designates *either* vacancies or interstitial ions, and these are called type A defects (by assumption, both are not present together in comparable numbers except near stoichiometry). Subscript M denotes cations of abnormal positive charge, hereafter called type M defects.

Each of the two coexisting defect assemblies is given its own set of spacing parameters, $C_A - i$ and $C_M - i$; these define the spacings between

type A and type M defects, respectively. Since the two types of defects interact, each spacing parameter now embraces more than one energy level. Specifically, a two-assembly system involves $C_M C_A$ possible levels. This large number can be reduced to $C_M + C_A$ by an idealization that over-simplifies the conditions in a real defect solid, but gives useful results.[1,2] The assumption is that despite the interactions between the two types of defects, each type is arranged independently on its own set of lattice sites. The present program embodies this assumption in the computation of the defect distributions in two-assembly systems.

II. DISTRIBUTION EQUATIONS AND DERIVED THERMODYNAMIC QUANTITIES

A. Distribution Equations

Equations for the distribution of two assemblies of defects, each on its own sublattice, have been developed in Reference (1). A simplified set of distribution equations consists of

$$\ell n\,(C_M - i) - \ell n \frac{y_i}{W_i^M} + \alpha_M - \frac{E_i}{1.987T} \sum_{j=i}^{L_M} \left(\frac{C_M - i}{C_M - j}\right) \ell n \left(1 - \frac{y_j}{W_j^M}\right) = 0$$

$$(i = 0, 1, \ldots, L_M); \qquad (1a)$$

$$E_i = \left(\frac{C_M}{C_M - i}\right)^{6/5} E_0; \qquad (1b)^*$$

$$W_i^M = \frac{1 + (C_M - i)\, y_i - \sum_{j=0}^{i} (C_M - j)\, y_j}{C_M - i}; \qquad (1c)$$

$$\sum_{i=0}^{L_M} y_i = \frac{Z_A}{Z_M} |X|; \qquad (1d)$$

$$\ell n\,(C_A - i) - \ell n \frac{x_i}{W_i^A} + \alpha_A - \frac{U_i}{1.987T} + \sum_{j=i}^{L_A} \left(\frac{C_A - i}{C_A - j}\right) \ell n \left(1 - \frac{x_j}{W_j^A}\right) = 0$$

$$(i = 0, 1, \ldots, L_A); \qquad (1e)$$

---

*This is a more accurate energy relation than is given in Reference (1).

$$U_i = \left(\frac{C_A}{C_A - i}\right)^{6/5} U_0; \tag{1f}$$

$$W_i^A = \frac{A + (C_A - i)\, x_i - \sum_{j=0}^{i} (C_A - j)\, x_j}{C_A - i}; \tag{1g}$$

$$\sum_{i=0}^{L_A} x_i = |X|. \tag{1h}$$

The variables X, T, Z_A, Z_M, U_0, E_0, y_i, x_i, and A in Eqs. (1) are defined in Table I; they represent physical properties of the system at equilibrium and, as such, should be distinguished from the control integers C_A, C_M, L_A, and L_M. C_M determines the maximum number of energy levels to be considered, and sets the *lower* limit of $|X|$ for which Eqs. (1) will be applicable. Specifically,

$$|X| \text{ (minimum)} = 1/C_M. \tag{2}$$

TABLE I. Variables Appearing in the Output and Their Definitions

Program Name	Variable Designation in Eqs. (1) and (5)	Definition of Variable
ZA, ZM	Z_A, Z_M	Absolute magnitude of the charge (in units of electron charge) on a defect of type A or M relative to the appropriate normal site.
EZERO, UZERO	E_0, U_0	The smallest accountable repulsion energy (in cal) on a single defect of type M or A.
SON	$S^0_{O_N}$	The standard entropy (in eu) of oxygen gas (molecular when N = 2 and atomic when N = 1).
EN	N	A constant that establishes the reference state of the gas as being either atomic (N = 1) or molecular (N = 2).
X	X	The deviation (in gram-atoms) of the composition from stoichiometry (always expressed in terms of the oxygen content).
T	T	Temperature (in °K).
CM, CA	C_M, C_A	The spacing parameters for defects of type M or A.
A	A	The total number of locations available at one time for occupation by type A defects divided by the corresponding number for type M defects.
FRACTION*	y_i, x_i	The fraction of the total concentration of the type M or A defects that occurs in level i at equilibrium.
DFRACTION/DX*	$\frac{\partial y_i}{\partial \lvert X\rvert}$, $\frac{\partial x_i}{\partial \lvert X\rvert}$	

TABLE I (Contd.)

Program Name	Variable Designation in Eqs. (1) and (5)	Definition of Variable
RATIO*	$\frac{y_i}{W_i^M}, \frac{x_i}{W_i^A}$	
XF*	-	The value of X derived from $\sum_{n=0}^{L} (y_n/\lambda)$ as distinguished from the input value.
ALPHA*	α_M, α_A	The chemical potential of interaction (in cal) for the type M or A defects divided by 1.987T.
EF	E_F	The energy (in cal) involved in forming a gram-atom of type A defects together with Z_A/Z_M gram-atoms of type M defects (all at infinite dilution), plus a corresponding increase or decrease in the oxygen content of the gas phase.
EAM	E_{AM}	The energy (in cal) involved in the pairwise interaction of a mole of defect pairs, each consisting of a type A and a type M defect.
NMME	$\sum_{i=0}^{L_M} y_i E_i$	The total energy (in cal) derived from repulsions among Z/Z' gram-atoms of type M defects.
NAAU	$\sum_{i=0}^{L_A} x_i U_i$	The total energy (in cal) derived from repulsions among 1 gram-atom of type A defects.
NAM	$8C_A\lvert X\rvert\left(\frac{Z_M}{Z_A}\right)^2 \frac{2}{A}$	The concentration (in moles per $\lvert X\rvert$ gram-atoms of type A defects) of the defect pairs described in EAM.
SONM, HONM, FONM	$S^M_{O_N}, H^M_{O_N}, F^M_{O_N}$	The relative partial molar entropy, enthalpy, and free energy of oxygen in the solid (in eu or cal) referred to either atomic oxygen gas (N = 1) or molecular oxygen gas (N = 2).
PON	$P(O_N)$	The partial pressure in atmospheres of atomic oxygen (N = 1) or molecular oxygen (N = 2) in the gas in equilibrium with the solid.
SM, SA	-	±NSM and ±NSA (the sign corresponds to the sign of X) are the separate composition-dependent configurational contributions (in eu) to SONM of the type M and A defects.
SE	$S_E(= \pm S_C + S_V)$	NS_E is the net contribution to SONM of configurational terms that are independent of $X(S_C)$, and vibrational terms derived from the introduction of oxygen into the solid (S_V).

*These variable names apply to the type M defects in the first output block and to the type A defects in the second block.

The summation limit L_M sets the *upper* limit of $|X|$ as follows:

$$|X| \text{ (maximum)} = \frac{1}{C_M - L_M}. \tag{3}$$

For consistency in the definition of the ground levels of repulsion energy, U_0 and E_0 should be set equal, whereupon the following relations hold:

$$C_A = AC_M\left(\frac{Z_A}{Z_M}\right)^6 \tag{4a}$$

and

$$L_A = AL_M\left(\frac{Z_A}{Z_M}\right)^6 . \tag{4b}$$

When a set of values is specified for X, T, E_0, U_0, A, C_M, C_A, L_M, and L_A, the program uses Eqs. (1) to compute the equilibrium values of α_M* and α_A*; (y_0/W_0^M), ..., $(y_{L_M}/W_{L_M}^M)$; y_0, ..., y_{L_M}; (x_0/W_0^A), ..., $(x_{L_A}/W_{L_A}^A)$; and x_0, ..., x_{L_A}. In addition, the program calculates the derivatives $\partial y_i/\partial|X|$ and $\partial x_i/\partial|X|$.

B. Thermodynamic Quantities

Results obtained from the solution of the distribution equations may now be applied to the calculation of thermodynamic quantities. It is assumed that the oxygen:metal ratio in the solid is altered only through the exchange of oxygen with the gas phase (i.e., the partial pressure of oxygen ($P(O_N)$) must be high compared to that of the metal or of any metal oxide molecule). Regardless of whether the type A defects are in the anion lattice (as in UO_{2+x}) or in the cation lattice (as in $Fe_{1-x}O$), the total number of cations in the system is taken to be constant, while the number of anions is allowed to vary. However, differences of crystal volume arising from the gain or loss of oxygen is assumed to be a factor that may be neglected. When the distributions are computed prior to the thermodynamic calculations, the defect structures typified by the compounds above must be carefully distinguished or an incorrect value of the constant A may be used in Eq. (1g). In certain cases, solving Eqs. (1) with different values of A and comparing the calculated thermodynamic quantities with known experimental values may provide evidence supporting one defect structure over the other.

Thermodynamic quantities of interest are the relative partial molar entropy ($S_{O_N}^M$), enthalpy ($H_{O_N}^M$), and free energy ($F_{O_N}^M$) of oxygen in the solid. Here, N is either one or two depending on whether atomic or molecular oxygen gas is chosen for the reference state. The appropriate relations are

*See Table I.

$$S^M_{O_N} = \pm 1.987N \left[\sum_{i=0}^{L_M} \frac{\partial y_i}{\partial |X|} \left\{ \ell n\,(C_M - i) - \ell n \frac{y_i}{W^M_i} + (C_M - i) \sum_{j=i}^{L_M} \ell n \left(1 - \frac{y_j}{W^M_j} \right) \Big/ (C_M - j) \right\} \right.$$

$$\left. + \sum_{i=0}^{L_A} \frac{\partial x_i}{\partial |X|} \left\{ \ell n\,(C_A - i) - \ell n \frac{x_i}{W^A_i} + (C_A - i) \sum_{j=i}^{L_A} \ell n \left(1 - \frac{x_j}{W^A_j} \right) \Big/ (C_A - j) \right\} \right]$$

$$+ NS_E - S^0_{O_N}; \tag{5a}$$

$$H^M_{O_N} = \pm N \left[E_F + 8C_A|X| \left(\frac{Z_M}{Z_A} \right)^2 \frac{2}{A} \cdot E_{AM} + E_0 \sum_{i=0}^{L_M} \frac{\partial y_i}{\partial |X|} \left(\frac{C_M}{C_M - i} \right)^{6/5} \right.$$

$$\left. + U_0 \sum_{i=0}^{L_A} \frac{\partial x_i}{\partial |X|} \left(\frac{C_A}{C_A - i} \right)^{6/5} \right]; \tag{5b}$$

$$F^M_{O_N} = 1.987T\ \ell n\ P(O_N) = H^M_{O_N} - TS^M_{O_N}; \tag{5c}$$

$$S_E = \pm S_C + S_V. \tag{5d}$$

Definitions for the variables E_F, E_{AM}, S_C, and S_V appear in Table I.

In Eqs. (5), (+) corresponds to either an excess of anions or a deficiency of cations, and (-) to the opposite set of conditions. The program uses (+) when the input value of X is positive and (-) when $X \leq 0$.

Given relevant parameters, the program determines E_{AM} and E_F from known values of $F^M_{O_N}$, using the corresponding solutions of Eqs. (1) and (5) at two sets of X and T values. These two sets may include the same temperature, but must contain distinct X values.

After E_{AM} and E_F have been determined, Eqs. (5) are used to calculate $S^M_{O_N}$, $H^M_{O_N}$, $F^M_{O_N}$, and $P(O_N)$ for each input value of X at each input temperature (the corresponding value of $S^0_{O_N}$ must be supplied). The number of X and T values to be processed are denoted respectively by NOX and NOTEM.

III. OPTIONAL PLOTTING OF $S^M_{O_N}$, $H^M_{O_N}$, AND $F^M_{O_N}$

The program is capable of producing graphs for $S^M_{O_N}$, $H^M_{O_N}$, and $F^M_{O_N}$ as a function of X, using a DD-80 film unit or the CALCOMP 580. If this plot option is exercised, the results have the scaling

$$-140 \leq S^M_{O_N} \leq 0,$$

$$-260000 \leq H^M_{O_N} \leq 0,$$

and

$$-180000 \leq F^M_{O_N} \leq 0.$$

Each curve represents behavior at a particular temperature; it consists of line segments joining points computed from the set of X values on CARD TYPE 5 (see Section IV).

A control block of input cards, which precedes the data, directs the plotting. Unless plotting is not desired (when the block comprises a single blank card), the following four cards are required: card 1 contains a single digit greater than 0 in column 3, and cards 2, 3, and 4 contain labels associated respectively with the curves for $S^M_{O_N}$, $H^M_{O_N}$, and $F^M_{O_N}$.

A SCOPE control card selects the destination of the graphs:

$^7_9$ EQUIP,5=SV causes the results to be put on a magnetic tape that is then sent to CALCOMP for processing.

$^7_9$ EQUIP,15=TV causes the results to be processed directly by the DD-80 film unit.

The CALCOMP-DD80 compatibility subroutine PRD-21-6 controls the graphs and must be included with this program.

IV. DATA INPUT CARDS REQUIRED

Following the plotting control cards described in the preceding section is a data card block consisting of

Card Type	No. of Cards	Format	Contents of Card
1	1	5D12.5	N, Z_A, Z_M, S_E, A
2	1	4I3	C_M, L_M, C_A, L_A
3	2	6D12.5	$S^0_{O_N}$, $F^M_{O_N}$, X, T, E_0, U_0 (two sets, to be used for the calculation of E_F and E_{AM})
4	1	2I3	NOX, NOTEM
5	$\left[\frac{NOX+5}{6}\right]$	6D12.5	X values, 6 to a card, or less on the last card (NOX distinct numbers must be supplied)
6	$\left[\frac{NOTEM+5}{6}\right]$	6D12.5	T values (NOTEM distinct numbers must be supplied)
7	$\left[\frac{NOTEM+5}{6}\right]$	6D12.5	$S^0_{O_N}$ values (one for each T value on CARD TYPE 6, and listed in the same sequence)

See Table II for a listing of sample input values for CeO_{2-X} [References (1) and (3)] and UO_{2-X} [References (2) and (4)].

TABLE II. Sample Values of Required Input Data

Program Name	Variable in Eqs. (1) and (5)	Sample Values		Program Name	Variable in Eqs. (1) and (5)	Sample Values	
		CeO_{2-X} (1)	UO_{2+X} (2)			CeO_{2-X} (1)	UO_{2+X} (2)
X	X	-0.04 to -0.34	0.04 to 0.28	LA	L_A	56	28
T	T	910 to 1600°K	1073 to 1600°K	N	N	2	2
EZERO	E_0	4000 to 5000	3000	SON	$S^0_{O_N}$	57.4 to 62.2*	58.8 to 62.2*
UZERO	U_0	4000 to 5000	3000	SE	S_E	3 to 4**	12.6 to 13.8†
A	A	2	1	FONM††	$F^{M\ (1)}_{O_N}$	-96300 (-0.1,1190)‡	-36900 (0.16,1373)
CM	C_M	30	30	FONM††	$F^{M\ (2)}_{O_N}$	-71100 (-0.06,1440)	-45900 (0.085,1373)
CA	C_A	60	30	ZM	Z_M	1	1
LM	L_M	28	28	ZA	Z_A	1	1

*See Reference (5).
**The value 0 was used in Reference (1), but calculations described in Reference (2) suggest that a vibrational component of about 4 would be a better approximation.
†These values consist of a composition-independent configurational quantity amounting to $1.987 \ln 12 + \ln 8$) plus a vibrational component varying between 3.5 and 4.7.(2)
††These two known values of FONM are required for the calculation of EF and EAM.
‡This is an abbreviation for -96,300 cal at X = -0.1 and T = 1190°K.

IV. DATA INPUT CARDS REQUIRED

Following the plotting control cards described in the preceding section is a data card block consisting of

Card Type	No. of Cards	Format	Contents of Card
1	1	8D12.5	N, Z_A, Z_M, S_U, A
2	1	4I12	C_M, I_M, C_A, I_A
3	2	6D12.5	S_{0N}^{M}, F_{0N}^{M}, X, T, E_0, U_0 (two sets to be used for the calculation of E_r and E_{AM})
4	1	2I3	NOX, NOTEM
5	$\left[\frac{NOX+5}{6}\right]$	6D12.5	X values, 6 to a card, or less on the last card (NOX distinct numbers must be supplied)
6	$\left[\frac{NOTEM+5}{6}\right]$	6D12.5	T values (NOTEM distinct numbers must be supplied)
7	$\left[\frac{NOTEM+5}{6}\right]$	6D12.5	S_{0N}^{M} values (one for each T value on CARD TYPE 6, and listed in the same sequence)

See Table II for a listing of sample input values for C_{60} [Reference (1) and (2)] and UO_2 [References (2) and (4)].

V. OUTPUT PRINTED BY THE PROGRAM

There are two types of printed output:

(1) Labelled values for the input variables $F^M_{O_N}$, N, S_E, A, Z_A, Z_M, E_0, U_0, $S^0_{O_N}$, X, T, C_M, C_A;

(2) Labelled values of the calculated variables XF, α, y_i or x_i, $\frac{\partial y_i}{\partial |X|}$ or $\frac{\partial x_i}{\partial |X|}$, Y_i/S_i, E_F, E_{AM}, S_M, S_A, $S^M_{O_N}$, $F^M_{O_N}$, $P(O_N)$, $H^M_{O_N}$, NAM, NAAU, NMME.

Symbols not defined previously are explained in Table I.

If a plotting option is chosen, the values $|X|$, $S^M_{O_N}$, $H^M_{O_N}$, and $F^M_{O_N}$ are printed for each point of the plot.

VI. METHOD OF SOLVING THE DISTRIBUTION EQUATIONS

Since Eqs. (1a) through (1d) have the same basic structure as (1e) through (1h), both sets can be expressed in the general form

$$\ell n\,(c - j) - \ell n\,\frac{y_j}{s_j} + \alpha - \frac{\epsilon}{(c - j)^{6/5}} + \sum_{k=j}^{L} \frac{c - j}{c - k}\,\ell n\left(1 - \frac{y_k}{s_k}\right) = 0, \qquad (j = 0, 1, \ldots, L),$$

$$s_k = \left[A + (c - k)\,y_k - \sum_{m=0}^{k} (c - m)\,y_m\right] \Big/ (c - k),$$

and

$$\sum_{n=0}^{L} y_n = \lambda |X|.$$

If $S_j = (c - j)\,s_j$ and $Y_j = (c - j)\,y_j$, these equations can be rewritten as

$$\ell n\,(c - j) - \ell n\,\frac{Y_j}{S_j} + \alpha - \frac{\epsilon}{(c - j)^{6/5}} + (c - j) \sum_{k=j}^{L} \frac{\ell n\,[1 - (Y_k/S_k)]}{c - k} = 0,$$

$$S_0 = A,$$

$$S_k = A - \sum_{m=0}^{k-1} Y_m,$$

and

$$\sum_{n=0}^{L} Y_n/(c-n) = \lambda|X|.$$

Consequently, $Y_j = S_j - S_{j+1}$ and

$$\ell n\,(c-j) - \ell n\left(1 - \frac{S_{j+1}}{S_j}\right) + \alpha - \frac{\epsilon}{(c-j)^{6/5}} + (c-j)\sum_{k=j}^{L} \frac{\ell n\,(S_{k+1}/S_k)}{(c-k)} = 0. \qquad (6)$$

If f_j represents the left side of Eq. (6), then

$$(c-j)\,f_{j-1} - (c+1-j)\,f_j = 0$$

and

$$(c-j)\,\ell n\,(c+1-j) - (c+1-j)\,\ell n\,(c-j) - (c-j)\,\ell n\left(1 - \frac{S_j}{S_{j-1}}\right)$$

$$+ (c+1-j)\,\ell n\left(1 - \frac{S_{j+1}}{S_j}\right) - \alpha + \epsilon\left\{\frac{c+1-j}{(c-j)^{6/5}} - \frac{c-j}{(c+1-j)^{6/5}}\right\}$$

$$+ (c-j)\,\ell n\,\frac{S_j}{S_{j-1}} = 0 \qquad (6a)$$

for $j = 1, 2, \ldots, L$.

If g_j represents the left side of Eq. (6a), then $(g_{j-1} - g_j)/(c+1-j) = 0$ yields

$$\mathrm{AlE}_j + 2\,\ell n\left(1 - \frac{S_j}{S_{j-1}}\right) - \ell n\left(1 - \frac{S_{j+1}}{S_j}\right) + \ell n\,\frac{S_{j-1}}{S_{j-2}} - \ell n\left(1 - \frac{S_{j-1}}{S_{j-2}}\right)$$

$$- \frac{c-j}{c+1-j}\,\ell n\,\frac{S_j}{S_{j-1}} = 0, \qquad (6b)$$

where

$$\mathrm{AlE}_j = \ell n\,\frac{(c+2-j)(c-j)}{(c+1-j)^2} + \epsilon\left[-(c+2-j)^{-6/5} + 2(c+1-j)^{-6/5} - (c-j)^{-6/5}\right],$$

for $j = 2, 3, \ldots, L$.

By setting j equal to L and assuming a numerical value for S_{L+1}/S_L we may solve Eq. (6) for α. Introduction of this result into Eq. (6a) determines S_L/S_{L-1}; the remaining values of S_j/S_{j-1} (for $j = L-1, L-2, \ldots, 2$) are then obtained from Eqs. (6b). Finally, on the basis that $Y_j = S_j - S_{j+1}$, $\sum_{n=0}^{L} Y_n/(c-n)$ is calculated and compared with $\lambda|X|$. This procedure is repeated in a bisection search that starts with a value of S_{L+1}/S_L in the interval (0, 1), and continues with new values of the ratio until $\sum_{n=0}^{L} Y_n/(c-n)$ approximates $\lambda|X|$.

After the distribution equations have been solved for y_j, the program proceeds to evaluate $\partial y_j/\partial|X| = y_j'$ (hereafter, primes indicate differentiation with respect to $|X|$).

Equations (6) and (6a) imply

$$\left\{-\ln Y_L + \alpha + \ln S_{L+1}\right\}' = 0$$

and

$$\left\{-(c-j)\ln Y_{j-1} + (c+1-j)\ln Y_j - \ln S_j - \alpha\right\}' = 0,$$

or

$$\left\{-\ln Y_L + \ln S_{L+1} - (c-j)\ln Y_{j-1} + (c+1-j)\ln Y_j - \ln S_j\right\}' = 0. \tag{6c}$$

Since $S_j - S_{j+1} = Y_j$, it follows that $S_0 - S_{j+1} = \sum_{k=0}^{j} Y_k$ and $S_{j+1}' = -\sum_{k=0}^{j} Y_k'$. Carrying out the differentiation of Eq. (6c) and replacing S_{j+1}' by the equivalent summation term give

$$-\left(Y_L'/Y_L\right) - \sum_{k=0}^{L}\left(Y_k'/S_{L+1}\right) - (c-j)\left(Y_{j-1}'/Y_{j-1}\right) + (c+1-j)\left(Y_j'/Y_j\right)$$

$$+ \sum_{k=0}^{j-1}\left(Y_k'/S_j\right) = 0 \tag{6d}$$

for $j = 1, 2, \ldots, L$.

The following condition must also be obeyed:

$$\sum_{n=0}^{L} Y'_n/(c-n) = \lambda. \tag{6e}$$

It is now possible to determine Y'_j from the system of L + 1 linear equations represented by Eqs. (6d) and (6e).

VII. SUGGESTIONS FOR ACCURACY CHECKS

In general, agreement between the left and right sides of the equation $\sum_{k=0}^{L} y_k = \lambda|X|$ is not exact even when 25 decimal figures are used in the approximation for S_{L+1}/S_L. This is a result of roundoff errors and the large number of equations commonly involved. The value for $|X|$ that appears in the printout with the label XF represents $\sum_{n=0}^{L} y_n/\lambda$. A comparison of XF with the input value of $|X|$ provides an estimate of the accuracy of the results.

The accuracy of y_j and $\partial y_j/\partial|X|$ can be checked by calculating them for a set of closely spaced X values (keeping the other parameters fixed); $\Delta y_j/\Delta|X|$ may then be compared to the corresponding true derivative.

VIII. PROGRAMMING NOTES

Because of the possibly large number of equations and the high probability of large truncation errors, this program is designed for double precision accuracy. If double precision is not required, the 5 cards that define TYPE DOUBLE should be removed and all references to DEXP and DLOG modified to EXPF and LOGF. In addition, all format specifications involving D type conversions should be changed to the corresponding E types.

If the plotting capability is not needed, the code can be started at statement 1001, and ended after statement 42 as follows:

```
      PØN = ...
      PRINT 4006, ..
    X EAM,EF
      INDEXY = INDEXY+1
      IF (INDEXY-NØX) 43,43,46
```

```
43    XCØMP  =  XSTØ (INDEXY)
      GØ TØ 4
46    ITCØ  =  ITCØ + 1
      IF (ITCØ-NØTEM) 41,41,47
47    CALL EXIT
      END
```

Formats 4007, 4008, 4009, and 4010 can then be eliminated, and the control block preceding the input data cards can be ignored. In addition, ARRAY (1000) is not needed and the PRD-21-6 plotting subroutine can be omitted.

The block of code beginning with

```
C     SOLVE SIMULTANEOUS EQUATIONS THAT DETERMINE
      DERIVATIVES
```

and ending with statement 2015 is logically equivalent to the routine MATINV, ANL F402.

This code is designed to operate with the CDC-3600 computer.

IX. ACKNOWLEDGMENT

The authors wish to express thanks to D. A. Woodward for noting that $\partial y_i / \partial |X|$ can be obtained by solving a set of simultaneous linear equations.

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```
13    XCOMP = XSTD (INDEXY)
      CG 1Q 1
14    ITCQ = ITCQ+1
      IF (ITCQ-NOTEM) 11,11,17
17    CALL EXIT
      END
```

Formats 1007, 1008, 1009, and 1110 can then be eliminated, and the control cards preceding the input data cards can be removed. In addition, ARRAY (1000) is not needed and the PRD-21-6 plotting subroutine can be omitted.

The block of code beginning with

```
C     SOLVE SIMULTANEOUS EQUATIONS THAT DETERMINE
C     DERIVATIVES
```

and ending with statement 2015 is logically equivalent to the routine MATINV, ANL 1402.

This code is designed to operate with the CDC-3600 computer.

IX. ACKNOWLEDGMENT

The authors wish to express thanks to D. A. Wrobewski for noting that $\det|X|$ can be obtained by solving a set of simultaneous linear equations.

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CODE LISTING

```
      PROGRAM E8207
C       A PROGRAM FOR THE STATISTICAL ANALYSIS OF DEFECTS IN NONSTOICHIOMETRIC
C                                   METAL OXIDES
      DIMENSION B(99,99),U(99),X(100),IA(99),IB(99),MP(99),VL(99),
     XYF(100),YH(100),YS(100),A1E(99),CLN(99),CON(99),RAS(99),LA1(6),
     XLA2(6),LA3(6),ROD(99),RON(99),SAT(99),YOS(99),CLOD(99),CLOG(99),
     XTSTO(99),VECS(99),VECY(99),WECY(99),XSTO(100),ARRAY(1000)
      TYPE DOUBLE B,U,VL,A1E,CLN,CON,RAS,ROD,RON,SAT,YOS,CLOD,CLOG,TSTO
     X,VECS,VECY,WECY,XSTO,A,E,P,T,W,AN,AT,EF,EN,ES,GH,GL,SA,SE,SM,SR,
     XTB,TE,TW,ZA,ZM,COB,CVN,EAM,ENA,PON,SFR,SON,TEE,XUM,CANT,CLAW,
     XCORN,ENAA,ENAM,ENMM,FONM,HONM,SEA1,SEA2,SINX,SOMN,YACS,ZERO,ALPHA,
     XCEVR1,EZERO,HCOMP,UZERO,XCOMP
 4000 FORMAT (6D12.5)
 4001 FORMAT (7H1ZA=   F18.9/7H0ZM=   F18.9/7H0EZERO=F18.9/7H0UZERO=F18.
     X9/7HOSON  =F18.9/7H0X=    F18.9/7H T    =F18.9)
 4002 FORMAT (24I3)
 4003 FORMAT (4H CM=I3,6H   CA=I3)
 4004 FORMAT (3D38.24)
 4005 FORMAT(*0   XF=*D38.24/*0ALPHA=*D38.24)
 4006 FORMAT (6H0X   =F19.9/6H T   =F19.9/6H SM  =F19.9/6H SA  =F19.9/6H
     X SE  =F19.9/6H SONM=F19.9/6H FONM=F19.9/14H -LOG(PON)/N= E19.9/6H
     XHONM=F19.9/6H NAM =F19.9/6H NAAU=F19.9/6H NMME=F19.9/6H EAM =F19.9
     X/6H EF  =F19.9)
 4007 FORMAT (6A8)
 4008 FORMAT (*1PLOT X,SOM2,HO2M,FO2M*)
 4009 FORMAT (4F20.3)
 4010 FORMAT (* SCALED TO*)
 4011 FORMAT (*1*)
 4012 FORMAT (*1FONM=*D38.24/*   N=*D38.24/*  SE=*D38.24/*    A=*D38.24)
 4013 FORMAT (16X,*FRACTION*,28X,*D FRACTION/DX*,29X,*RATIO*)
 4014 FORMAT (* EF,EAM*)
      READ 4002,IPLOT
      IF (IPLOT) 1001,1001,1000
 1000 READ 4007,(LA1(K),K=1,6)
      READ 4007,(LA2(K),K=1,6)
      READ 4007,(LA3(K),K=1,6)
      CALL PLOTS(ARRAY,1000,15)
 1001 ZERO=0
      W=1
      TW=2
      DO1K=1,99
      CON(K)=E=K
      A=W/E
      RON(K)=A**1.2
    1 CLOG(K)=CLOG(E)
      DO2I=2,98
      CLOD(I)=CLOG(I+1)-TW*CLOG(I)+CLOG(I-1)
    2 ROD(I)=-RON(I+1)+TW*RON(I)-RON(I-1)
      CVN=1.987
      HCOMP=DEXP(-CON(23)*CLOG(10))
      YACS=1000000.
      MUMP=-1
C      AT SYMBOL IN THE CODE CORRESPONDS TO A IN EQUATION 1G
C      MW=CM,    LWON=LM,    M2=CA,     LTWO=LA
      READ4000,EN,ZA,ZM,SE,AT
      READ4002,MW,LWON,M2,LTWO
      CLAW=-CLOG(10)*EN
    3 READ 4000,SON,FONM,XCOMP,T,EZERO,UZERO
      PRINT 4012,FONM,EN,SE,AT
    4 PRINT4001,ZA,ZM,EZERO,UZERO,SON,XCOMP,T
      PRINT4003,MW,M2
      CORN=CVN*T
      CANT=EZERO/CORN
      COB=ZA/ZM
      ENA=8*M2
      ENAM=XCOMP*ENA/COB**2*TW/AT
      M1=MW
      LEE=LWON
      SINX=W
      VECS(1)=W
      JUMP=-1
      IF(XCOMP)5,5,6
    5 SINX=-W
      XCOMP=-XCOMP
```

```
      ENAM=-ENAM
C      START SOLUTION OF EQUATIONS 6
    6 TEE=CANT/RON(M1)
      M1M=M1-1
      M1P=M1+1
      DO7J=2,M1M
      ME=M1P-J
      A1E(J)=CLOD(ME)+TEE*ROD(ME)
    7 CLN(J)=-CON(ME-1)/CON(ME)
    8 L1=LEE
      L1P=L1+1
      M=M1-L1
      SFR=CLOG(M)-TEE*RON(M)
      SR=-CON(M+1)*SFR+CON(M)*(CLOG(M+1)-TEE*RON(M+1))
      GH=W
      GL=ZERO
    9 ES=(GL+GH)/TW
   10 LE=L1P
C      ES CORRESPONDS TO 1-Y(L)/S(L)=S(L+1)/S(L)
C      RAS(I) CORRESPONDS TO S(I)/S(I-1)
C      YOS(I) CORRESPONDS TO Y(I-1)/S(I-1)
C      RAS(I)=1-YOS(I)
C      VL(I) CORRESPONDS TO  LN (1-Y(I-1)/S(I-1) )
      RAS(LE)=E=ES
      YOS(LE)=W-E
      VL(LE)=DLOG(E)
      A=-DLOG(YOS(LE))
      ALPHA=-SFR-VL(LE)-A
      LE=LE-1
      MU=M1-LE
      TE=DEXP((-SR+A*CON(MU+1)+ALPHA)/CON(MU))
   11 AN=W+TE
      RAS(LE)=E=TE/AN
      YOS(LE)=W/AN
      IF(AN-YACS) 13,13,12
   12 TE=YOS(LE)
      XUM=TE**2
      VL(LE)=-XUM/CON(4)*(TW+XUM)-TE/CON(15)*((XUM*CON(3)+CON(5))*XUM+CO
     XN(15))
      GO TO 14
   13 VL(LE)=DLOG(E)
   14 IF(LE-1) 16,16,15
   15 TE=YOS(LE+1)/YOS(LE)**2*DEXP(-A1E(LE)-CLN(LE)*VL(LE))
      LE=LE-1
      GO TO 11
   16 XUM=ZERO
      DO  17  KL=1,L1P
      VECS(KL+1)=RAS(KL)*VECS(KL)
      VECY(KL)=VECS(KL)*YOS(KL)
      WECY(KL)=VECY(KL)/CON(M1P-KL)
   17 XUM=XUM+WECY(KL)
      XUM=XUM/COB
      IF(XUM-XCOMP) 18,21,19
   18 GH=ES
      GO TO 20
   19 GL=ES
   20 IF((GH-GL)/GH-HCOMP) 21,21,9
C      END SOLUTION OF EQUATIONS 6
C      START DETERMINATION OF DERIVATIVES
   21 TE=-W/VECS(L1P+1)
      DO  22  K6=1,L1P
      U(K6)=ZERO
C      RESCALE VL FOR LATER USE IN LOOP 34
      VL(K6)=VL(K6)/CON(M1P-K6)
   22 B(1,K6)=TE
      B(1,L1P)=-W/VECY(L1P)+B(1,L1P)
      DO  23  L8=1,L1P
      TE=B(1,L8)
      DO  23  K8=2,L1
   23 B(K8,L8)=TE
      DO  25  L10=1,L1
      LY=L10+1
      B(L10,L10)=B(L10,L10)-CON(M1-L10)/VECY(L10)
      B(L10,LY)=B(L10,LY)+CON(M1P-L10)/VECY(LY)
      TE=W/VECS(LY)
      DO  24  N10=1,L10
   24 B(L10,N10)=B(L10,N10)+TE
```

```
   25 CONTINUE
      U(L1P)=CCB
      DO  26  L9=1,L1P
   26 B(L1P,L9)=W/CON(M1P-L9)
C      SOLVE SIMULTANEOUS EQUATIONS THAT DETERMINE DERIVATIVES
      NDIM=L1P
      DO 2000 J2000=1,NDIM
 2000 MP(J2000)=0
      DO 2012 I2012=1,NDIM
      A=ZERO
      DO 2005 J2005=1,NDIM
      IF (MP(J2005)-1)2001,2005,2001
 2001 DO 2004 K2004=1,NDIM
      IF (MP(K2004)-1)2002,2004,33
 2002 P=B(J2005,K2004)
      IF ((A-P)*(A+P)) 2003,2004,2004
 2003 IR=J2005
      IC=K2004
      A=P
 2004 CONTINUE
 2005 CONTINUE
      MP(IC)=MP(IC)+1
      IF (IR-IC)2006,2008,2006
 2006 DO 2007 L2007=1,NDIM
      A=B(IR,L2007)
      B(IR,L2007)=B(IC,L2007)
 2007 B(IC,L2007)=A
      A=U(IR)
      U(IR)=U(IC)
      U(IC)=A
 2008 IA(I2012)=IR
      IB(I2012)=IC
      A=B(IC,IC)
      B(IC,IC)=W
      DO 2009 L2009=1,NDIM
 2009 B(IC,L2009)=B(IC,L2009)/A
      U(IC)=U(IC)/A
      DO 2012 L2012=1,NDIM
      IF (L2012-IC)2010,2012,2010
 2010 A=B(L2012,IC)
      B(L2012,IC)=ZERO
      DO 2011 L2011=1,NDIM
 2011 B(L2012,L2011)=B(L2012,L2011)-B(IC,L2011)*A
      U(L2012)=U(L2012)-U(IC)*A
 2012 CONTINUE
      DO 2015 I2015=1,NDIM
      L2015=NDIM+1-I2015
      IF (IA(L2015)-IB(L2015))2013,2015,2013
 2013 JR=IA(L2015)
      JC=IB(L2015)
      DO 2014 K2014=1,NDIM
      A=B(K2014,JR)
      B(K2014,JR)=B(K2014,JC)
 2014 B(K2014,JC)=A
 2015 CONTINUE
C      END SOLUTION OF SIMULTANEOUS EQUATIONS
   33 P=ZERO
      DO  35  L13=1,L1P
      MU=M1P-L13
      U(L13)=U(L13)/CON(MU)
      E=ZERO
      DO  34  M14=L13,L1P
C      VL WAS RESCALED IN LOOP 22
   34 E=E+VL(M14)
   35 P=P+(CON(MU)*E+CLOG(MU)-DLOG(YOS(L13)))*U(L13)
      SA=P*CVN
      PRINT 4005,XUM,ALPHA
      PRINT 4013
      PRINT 4004,(WECY(KL5),U(KL5),YOS(KL5),KL5=1,L1P)
      ENAA=ZERO
      DO  36  M201=1,L1P
      LB=M1+1-M201
      TB=RON(LB)
   36 ENAA=ENAA+U(M201)*TB
      ENAA=ENAA/RON(M1)
      IF (JUMP) 37,38,38
```

```
37 JUMP=1
   ENMM=ENAA*EZERO
   SM=SA
   VECS(1)=AT
   LEE=LTWC
   M1=M2
   COB=W
   CANT=UZERO/CORN
   GO TO 6
38 ENAA=ENAA*UZERO
   SOMN=EN*(SINX*(SM+SA)+SE)-SON
   XCOMP=XCCMP*SINX
   SEA2=(FONM+T*SOMN)/EN*SINX-ENAA-ENMM
   IF (MUMP) 39,40,42
39 SEA1=SEA2
   CEVR1=ENAM
   MUMP=0
   GO TO 3
40 EAM=(SEA1-SEA2)/(CEVR1-ENAM)
   EF=-CEVR1*EAM+SEA1
   PRINT4014
   PRINT 4004,EF,EAM
   MUMP=1
   READ 4002,NOX,NOTEM
   READ 4000,(XSTO(I),I=1,NOX)
   READ 4000,(TSTO(I),I=1,NOTEM)
   READ4000,(SAT(I),I=1,NOTEM)
   ITCO=1
41 T=TSTO(ITCO)
   PRINT 4011
   INDEXY=1
   XCOMP=XSTO(1)
   SON=SAT(ITCO)
   GO TO 4
42 HONM=SINX*EN*(EF+ENAM*EAM+ENAA+ENMM)
   FONM=HONM-SOMN*T
   PON=FONM/CORN/CLAW
   PRINT 4006,XCOMP,T,SM,SA,SE,SOMN,FONM,PON,HONM,ENAM,ENAA,ENMM,
  XEAM,EF
   X(INDEXY)=XCOMP*SINX
   YS(INDEXY)=SOMN
   YH(INDEXY)=HONM
   YF(INDEXY)=FONM
   INDEXY=INDEXY+1
   IF (INDEXY-NOX) 43,43,44
43 XCOMP=XSTO(INDEXY)
   GO TO 4
44 IF (IPLCT.LE.0) GOTO46
   PRINT 4008
   PRINT 4009,(X(IN),YS(IN),YH(IN),YF(IN),IN=1,NOX)
   DO45K=1,NOX
   X(K)=25.*X(K)
   YS(K)=-YS(K)/14.
   YH(K)=-YH(K)/26000.
45 YF(K)=-YF(K)/18000.
   CALL AXIS(0.,0.,LA1,-48,10.,0.,0.,.04)
   CALL AXIS(0.,0.,1H ,1,10.,90.,0.,.1)
   CALL LINE(X,YS,NOX,1)
   CALL PLCT(20.,0.,-3)
   PRINT 4010
   CALL AXIS(0.,0.,LA2,-48,10.,0.,0.,.04)
   CALL AXIS(0.,0.,1H ,1,10.,90.,0.,.1)
   CALL LINE(X,YH,NOX,1)
   CALL PLCT(20.,0.,-3)
   PRINT 4009,(X(IN),YS(IN),YH(IN),YF(IN),IN=1,NOX)
   CALL AXIS(0.,0.,LA3,-48,10.,C.,0.,.04)
   CALL AXIS(0.,0.,1H ,1,10.,90.,0.,.1)
   CALL LINE(X,YF,NOX,1)
   CALL PLCT(20.,0.,-3)
46 ITCO=ITCC+1
   IF (ITCC-NOTEM) 41,41,47
47 CALL EXIT
   END
```

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