THE USE OF COMPUTERS IN MATERIALS AND METALLURGICAL ENGINEERING EDUCATION

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ABSTRACT

During the past two years faculty members of the Materials and Metallurgical Engineering curricula have been taking an active part in computing work at The University of Michigan.

All undergraduate students in these curricula are now required to take an introductory sophomore-level computer course taught by Computing Center and Department of Mathematics personnel. Digital and analog computer work has been assigned in seven departmental courses during the past year, giving students an opportunity to gain practice in the application of computers to the solutions of their engineering problems. A description of the curricula and a discussion of computer use in the classroom are included.

This report also contains a selected set of nine example problems appropriate for classroom use prepared by departmental faculty. These may be considered as a supplement to the 87 example engineering problems, including several related to the materials and metallurgical subject area, which have been published previously by the Project.

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USE OF COMPUTERS IN MATERIALS AND METALLURGICAL ENGINEERING EDUCATION

I. INTRODUCTION

This report presents a set of problems which are suitable as assignments in undergraduate curricula in metallurgical and/or materials engineering. The curricula are outlined briefly to indicate the student's background and course sequences. A discussion of the computer experience in these undergraduate engineering curricula is included, citing both the advantages and limitations. The work covered in this report is a direct result of studies sponsored by The Ford Foundation at The University of Michigan on "The Use of Computers in Undergraduate Engineering Education." (See References 1, 2, 3).

II. THE STUDENT AND CURRICULA

During the past several years a course has been developed in the Mathematics Department at The University of Michigan which introduces the sophomore student to the principles of computer programming. This one credit hour course (Math 373), which is described in more detail in Reference 4, presents the introductory elements of computer organization and acquaints the student with programming procedures through the use of a formal computer language, MAD (Michigan Algorithm Decoder) (See Reference 5). This language is particularly suited for use at a university computing installation. Its use is relatively widespread and it is sufficiently similar to other available languages (e.g., FORTRAN, ALGOL, etc.), that the student has no major difficulty reorienting himself to other commonly used languages and systems which he may encounter in industry.

In the introductory computer course the student solves four problems on the computer. These are normally related to numerical topics such as 1.) finding the roots of polynomial and transcendental equations, 2.) interpolation using Lagrange's or Newton's formula, 3.) Gauss-Jordan reduction of a series of simultaneous linear equations, and 4.) least squares polynomial fitting. The above problems obviously do not make the student an expert. However, they do provide him with the basic computer training required to allow him to handle the computer problems in stoichiometry, thermodynamics, and rate processes which will be described later. Thus, the student is quickly in a position to use the computer on problems he would be required to solve in his normal course of studies, and a minimum of time is required in computer instruction for the computer's sake.

The requirements for the two curricula, metallurgical engineering and materials engineering are given in Table IE. As might be expected, these two curricula are very similar, particularly in their main stems, or "principles" courses. Figure IEa presents the processing stem of the common part of the two curricula, with an indication of the approximate semester for the scheduling of each course. Although the course label may not be identical with offerings in

other schools, the general goals are comparable. The "Introduction to Engineering Calculations," is primarily material and energy balances. "Thermodynamics" provides an introduction to the several laws with emphasis on property relationships. "Rate Processes" is a unified study of heat, mass, and energy transfer, and introduces chemical kinetics. The latter two courses have integrated laboratories.

The materials stem parallels the processing stem as shown in Figure IEb. The "Structure of Solids" course follows physical chemistry and is basically a solid state physics course designed for engineers. The balance of the materials courses are described sufficiently well by the indicated course titles. These are taken during the final year after the student has studied the full background of fundamentals.

TABLE IE

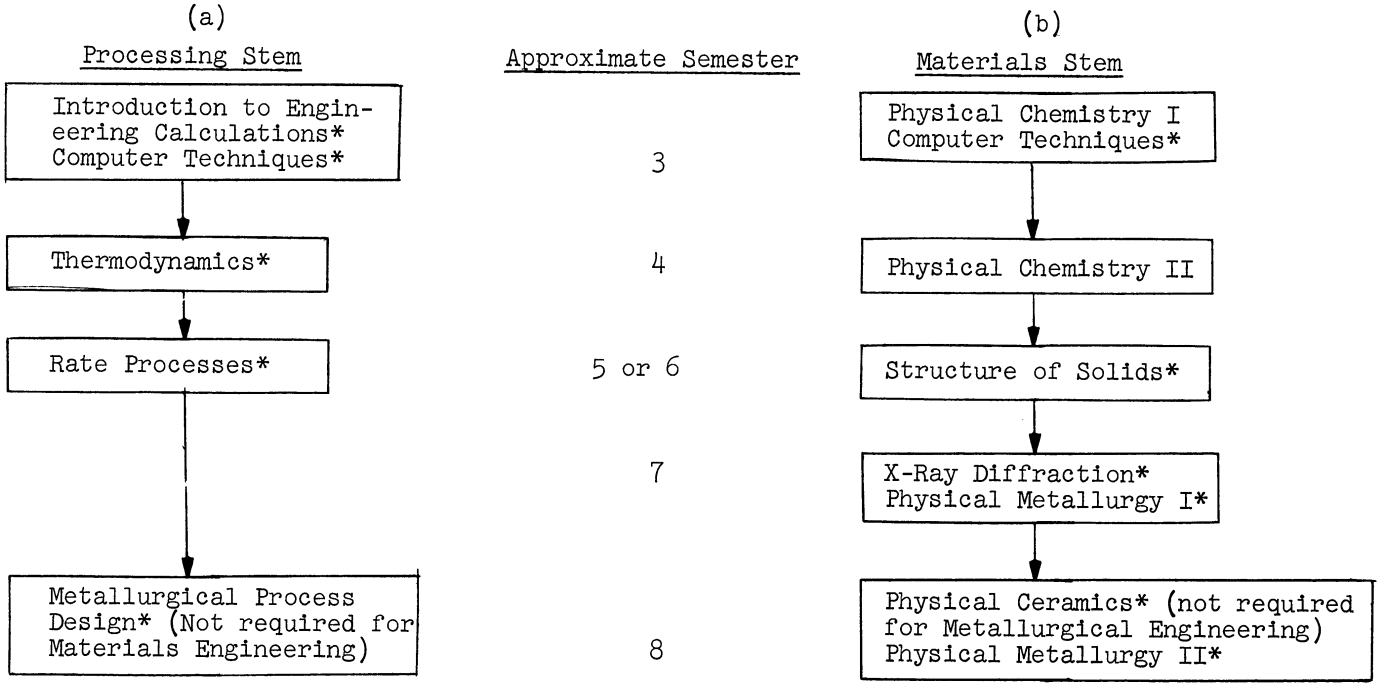
Curricula Requirements

B.S.E. (Materials Engineer)	Credit	B.S.E. (Metallurgical Engineer)	Credit
Courses Common to All Engineers:	43	Courses Common to All Engineers:	43
Computing Techniques*	1	Computing Techniques*	1
Advanced Chemistry	17 or 18	Advanced Chemistry	15
Advanced Science	4 or 5	Advanced Science	7
Engineering Cognates (Including Mechanics and Circuits)	14	Engineering Cognates	14
Humanities, Social Sciences, Arts, etc.	16	Humanities, Arts, etc.	14
		Economics	6
Thermodynamics and Rate Processes		Thermodynamics and Rate Processes	
Introduction to Engr. Calculations*	3	Introduction to Engr. Calculations*	3
Thermodynamics*	5	Thermodynamics*	5
Rate Processes*	5	Rate Processes*	5
Electives	2	Separations	3
Materials		Materials	
Structure of Solids*	3	Structure of Solids*	3
X-Ray Diffraction*	3	X-Ray Diffraction*	3
Physical Metallurgy*	7	Physical Metallurgy*	7
Physical Ceramics*	4		
Polymers	4	Metals Processing	
Engineering Design	6	Processing of Cast Metal	2
		Process Design*	4
		Electives	3

* Courses in which computer problems have been introduced.

Figure IE

Sequences for Stem Courses Utilizing Computer Problems
(* indicates computer problems have been introduced)



III. SELECTING ENGINEERING PROBLEMS FOR COMPUTER SOLUTION

It seems appropriate to select computer oriented problems for materials and metallurgical engineering courses which enhance training in two areas primarily: 1.) understanding engineering principles, and 2.) implementing design optimization. The example problems included in section VI represent such a selection with the above goals in mind and result in the development of two major categories of problems. The first category includes relatively simple problems requiring for their solutions either manual or computer procedures which are repetitive in character. Admittedly, in some cases, these problems may require more time to program and completely check out on the computer than to solve manually by traditional procedures. However, the computer requires a sufficiently greater accuracy of thinking on the part of the student so that only one problem may need to be assigned on a topic rather than two or more. The calculation of furnace efficiency (Problem 88) is an example of this type of problem.

The second category of computer usage does not involve the programming process but does require the student's knowledge of programming. This is illustrated in the diffusion problem (Problem 89) which is preprogrammed for the class, but requires the student to provide appropriate data for the correct solution. Thus, if the student is to determine carbon diffusion into steel he must define suitable starting and terminal conditions. The computer then makes the calculation

and supplies a more complete answer than could be demanded otherwise, with the consequence of better teaching illustrations. This particular problem has the further advantage that the dual use emphasizes the importance of the essential gradients and mobilities upon the unsteady-state transfer, whether it be energetic or atomic in character.

This second category of preprogrammed computer usage in class may be incorporated into a course for another purpose as illustrated by the problem on ionic crystal structure (Problem 92). The purpose in assigning this problem is to have the student gain a better understanding of the several simpler ionic structures. More specifically, the student must understand these structures if he is to provide the appropriate data for the calculations. Following this, the computer calculates the Madelung Constant which provides a positive check on the student's work. This particular problem is also programmed so that this student may analyze his error if he receives an incorrect answer.

IV. DISCUSSION OF COMPUTER USE

This discussion assumes that the instructor has taken time to develop a familiarity with the computer so that he may be able to effectively use the computer himself. The use of computers at the undergraduate level is not recommended unless this familiarity on the part of the instructor exists. Beyond the above limitation there is one major disadvantage and there are four advantages which can be cited for the use of computers at the undergraduate level.

The disadvantage of computer usage is the tendency on the part of the instructor to let the computer monopolize the time of the student in the class. Since the computer often becomes fascinating to both instructor and student, and since the number of problems suitable for solution using the computer is great, the instructor must "lean over backwards" to keep a balance in his course.

The advantages of computer usage in the areas of materials and metallurgical engineering include the following:

1. There is an opportunity to acquaint the future engineer with a tool which certainly will receive wide usage during the course of his professional life. It is difficult to imagine that this basic knowledge will not be desirable in either an engineering or management position of tomorrow.
2. Computer programming requires the student to synthesize a problem solution as well as to analyze the situation. Therefore, there are advantages in the incorporation of computer-oriented problems so that the student may experience more training in synthesis skills which are unique to engineering curricula. The student soon realizes that his solution must be a rigorous one. An attempt to "second guess" the professor usually fails at this point.

3. Simple but time consuming optimization problems can be incorporated into design courses. This particular advantage is most apparent in the processing courses within the metallurgical and materials engineering curricula. However, it is anticipated that this aspect will become more significant in the future in other courses as well.
4. Through the use of problems whose solutions have been preprogrammed, the student may be required to consider problems which are impossible in normal assignments.

V. CONCLUSIONS

The advantages of introducing the computer into the undergraduate engineering curricula outweigh the disadvantages, particularly when consideration is given to the fact that today's student will be serving his professional life in a technical and management situation where the computer will be even more important than it is today. A major advantage is the increase in synthesis aspects of the engineering training. Finally, time consuming and repetitive problems which have been bypassed in the past may be used.

The use of the computer is not recommended unless the instructor familiarizes himself with the computer's potentialities and limitations. This familiarity implies that the instructor can program his own problems, analyze his own errors, etc.

Care must be taken by the instructor so that his enthusiasm for computers does not permit an imbalance in the courses where computers are used.

VI. EXAMPLE PROBLEMS

Since the beginning of the Project on the Use of Computers in Engineering Education, a number of participants have prepared solutions for example problems of their own choosing which they felt would be suitable for use in a classroom at the graduate or undergraduate level. Nine complete solutions of problems which have been used in undergraduate classes are included in this section. They are listed in Table IIE. All of the digital computer programs which were required in the solution of the problems, were programmed in the MAD (Michigan Algorithm Decoder) language, which is described in a number of places, including Reference 5.

TABLE IIE

List of Example Problems

Number*	Title	Author	Page
88	Furnace Efficiency as a Function of Stack Gas Temperature	B. Carnahan	E9
89	Mass or Heat Transfer by Diffusion	M. J. Sinnott	E15
90	Predicting the Scrap Requirement for the Oxygen-Steel Converting Process	R. D. Pehlke	E19
91	Precision Lattice Parameter Determination for a Cubic Material	J. V. Gluck	E30
92	Ionic Crystal Structure	L. H. Van Vlack	E40
93	Unsteady State Heat Conduction in a Solidifying Alloy	J. R. Street and J. O. Wilkes	E51
94	Cooling of Pig Iron in a Transfer Ladle	R. D. Pehlke	E58
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96	Digital Computer Analysis of Galvanic Cell Data	R. D. Pehlke and K. J. Guion	E71

* These problems may be considered as a supplement to problems 1 through 87 published in previous reports of the Project.

In addition to the problems presented here, several others related to materials or metallurgical engineering subject areas are included among the 87 problems previously published by the Project. In particular, see Problems 1, 2, 3, 4, 5, 13, 14, and 17 in Reference 1, and Problem 47 in Reference 2.

The authors wish to acknowledge the contributions of several engineering faculty members in preparation of these problems. Several classes of students are to be thanked as well, particularly for their tolerance and interest during this early phase of computer integration into engineering course work. Finally the authors wish to thank the Project for its support and assistance in providing the necessary computer experience and also for help in preparing and reproducing this manuscript.

Example Problem No. 88

FURNACE EFFICIENCY AS A FUNCTION OF STACK GAS TEMPERATURE

by

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Course: Introduction to Engineering Calculations Credit hours: 3 Level: Sophomore

Statement of Problem

The burner of a domestic gas furnace is adjusted to use 20% excess air over that theoretically required for complete combustion. Write a MAD program which will prepare a table relating the efficiency of the furnace to the stack gas temperature at 200 degree intervals beginning at 70°F.

It may be assumed that the natural gas consists of pure methane (CH_4), that the inlet air of 50% relative humidity has a temperature of 70°F, and that reaction is complete at all temperatures.

Solution

Combustion proceeds according to the reaction

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O\ (g) + Q_R \qquad (1)$$

or that 1 mole of methane reacts with 2 moles of oxygen to yield 1 mole of carbon dioxide and 2 moles of water vapor with a release of heat Q_R. The percent efficiency can be calculated as eff. (%) = $(Q_F/Q_R)\times(100)$ where Q_F is the amount of heat absorbed by the furnace per mole of methane burned and is equal to the total amount available, Q_R, minus the heat content of all product gases relative to the inlet temperature. If we denote the heat carried away by the product gases as Q_P, then the efficiency can be written as

$$\text{eff.}(\%) = \frac{Q_R - Q_P}{Q_R}\times(100) \qquad \text{where} \qquad (2)$$

$$Q_P = \sum_{i=1}^{N} \left[\bar{c}_{p_i} \ (\Delta t) \right] \ m_i \qquad \text{where } \bar{c}_{p_i} \qquad (3)$$

is the average specific heat of the ith component gas in the product mixture of N gases, m_i is the number of moles of component i, and $\Delta t=(T-TZ)$ where T is the stack gas temperature and TZ is the inlet feed gas temperature. Since the specific heats for the product gases vary as functions of temperature, Q_P may be written more accurately as

$$Q_P = \sum_{i=1}^{N} \left[\int_{t=TZ}^{t=T} c_{p_i}(t)\ dt \right] m_i \qquad (4)$$

Furnace Efficiency as a Function of Stack Gas Temperature

A mass balance for the system based on one lb.-mole of methane is tabulated below where PCXS is the percent excess air in the entering mixture, and W_a is the lbs. H_2O/lb. dry air.

Component	Into System	Out of System
CH_4	1.0 moles	0.0 moles
O_2	2.0(100+PCXS)/100	2.0(PCXS/100)
N_2	2.0(100+PCXS) (79/21)/100	2.0(100+PCXS)(79/21)/100
H_2O	W_a(100+PCXS)2.0*29.0/(18.*100)	2.0+H_2O into system
CO_2	0.0	1.0

Data required for the solution of the problem is as follows:

1.) Q_R, the heat of combustion at 70°F.

2.) c_{p_i}, specific heat as a function of temperature for the four components in the stack gases.

3.) W_a, the pounds of water per pound of dry air for the indicated relative humidity of the inlet air.

The standard heat of combustion for methane is found to be [1] 51,571.4 Btu./lb. or 344,032 Btu./lb.-mole of methane at 25°C (77°F). Assume that the heat of combustion at 70°F is the same as at 77°F.

The specific heats of the four product gases as functions of temperature are as follows:[2]

O_2, $c_p = 8.27 + 0.000258t - 187700/t^2$

N_2, $c_p = 6.50 + 0.00100t$

H_2O, $c_p = 8.22 + 0.00015t + 0.00000134t^2$

CO_2, $c_p = 10.34 + 0.00274t - 195500/t^2$

where t is in °K, and c_p is in cal./ (°K gm-mole.)

W_a for an air temperature of 70°F and relative humidity of 50% is given as 0.017 lb. water/l dry air.[3]

Calculation of Q_P

In order to permit iterative calculation of Q_P, a general c_p equation of the form

$$c_{p_i} = a_i + b_i t + c_i t^2 + d_i/t^2$$

is used. Thus the coefficients for 4 product gases are as follows:

Comp.	i	a	b	c	d
O_2	1	8.27	0.000258	0.0	-187700
N_2	2	6.50	0.00100	0.0	0.0
H_2O	3	8.22	0.00015	0.00000134	0.0
CO_2	4	10.34	0.00274	0.0	-195500

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1. Perry, John H., Chemical Engineers Handbook, McGraw Hill, Inc., New York; 3rd edition, 1950, p. 244.

2. Ibid.; pp. 210-212.

3. Brown, G.G., Unit Operations, Wiley and Sons, New York, 1953, p. 545.

The integration required in Equation (4) can then be determined as

$$\int_{t=TZ}^{t=T} c_{p_i}(t)\,dt = \int_{t=TZ}^{t=T} (a_i+b_i t + c_i t^2 + d_i/t^2)dt \qquad (5)$$

$$= a_i\,(T-TZ)+b_i\,(T^2-TZ^2)/2+c_i\,(T^3-TZ^3)/3+d_i\,(\tfrac{1}{TZ} - \tfrac{1}{T})$$

In MAD notation this would be written as

```
A(I)*(T-TZ)+B(I)*(T.P.2-TZ.P.2)/2.+C(I)*(T.P.3-TZ.P.3)/3+D(I)*(1./TZ-1./T)     (6)
```

Since the constants given above are for temperature in ^{o}K, T and TZ must be in ^{o}K. The result of the integration will then be in units of cal./(gm-mol.^{o}K) which can be converted to English units (BTU/ lb.- mol.^{o}R) by multiplying by 1.8.

If we then let m_i in Equation (4) be represented by MOLOUT(I) in MAD notation, the total heat (in BTU's) carried away by component i is given by

```
(A(I)*(T-TZ)+B(I)*....etc.)*1.8*MOLOUT(I)                                    (7)
```

Evaluating this expression for all values of I(I=1,2,3,4) yields the contribution of O_2, N_2, H_2O, and CO_2 respectively to the sum in Equation (4). These contributions can be added into a variable location (HTCAP) as they are calculated, so that after the summing operation is completed HTCAP will contain Q_P, the total heat carried away by all gases leaving the stack.

A flow diagram for the solution of the problem and a listing of the MAD program are given on the following pages. The MAD program listing is discussed below.

Variable names in the program are as follows:

A	Array of 4 constants for the specific heat equation, i.e., a_1,a_2,a_3,a_4
B	Array of 4 constants for the specific heat equation, i.e., b_1,b_2,b_3,b_4
C	Array of 4 constants for the specific heat equation, i.e., c_1,c_2,c_3,c_4
D	Array of 4 constants for the specific heat equation, i.e., d_1,d_2,d_3,d_4
MOLOUT	Array containing values of m_i (Equation (4))
PCXS	Percent excess air
DELT	Increment in ^{o}F for preparing the table of stack gas temperature vs. efficiency
TZ	Inlet feed gas temperature in ^{o}K.
TF	Stack gas temperature in ^{o}F.
T	Stack gas temperature in ^{o}K.
HTCAP	Variable which is used to keep the partial sum in Equation (4)

The values of A(1), A(2), A(3), and A(4) are preset in memory by means of the VECTOR VALUES A(1) = statement.

The executable portion of the program begins with the statement labeled START. The first statement causes one data card to be read containing the values of PCXS and DELT which is the increment in temperature to be used for the tabulation of efficiencies. The four statements which follow calculate the moles of the various components per mole of methane in the product mixture. MOLOUT(1), (2), (3), (4) are the moles of the various components O_2, N_2, H_2O and CO_2.

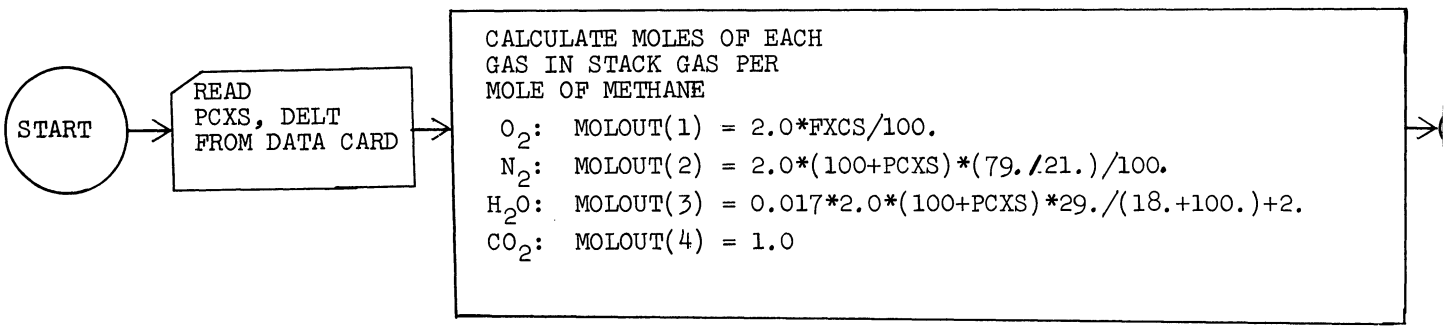
The PRINT statement which follows merely prints out the value of PCXS and the number of moles of the four components in the stack gases. TZ is the inlet temperature, 70°F, in °K. The iteration loop starting with THROUGH LAST and ending with the statement labeled LAST is the loop which prepares the table. TF is the temperature (in °F) which begins at 70 and is incremented by an amount DELT each time until TF $>$ 5000. The first statement inside the iteration loop determines T which is TF in °K.

The statement HTCAP=0 simply clears the storage location where the partial sum to determine Q_P will be saved. Q_P is calculated in the 2 statements starting with THROUGH SUM and ending with the statement labeled SUM. If Q_P (in location HTCAP after the THROUGH loop is completed) is greater than Q_R (344032), the table is finished and the program transfers back to the statement labeled START to read new values of PCXS and DELT. If HTCAP is not greater than 344032, a one line table entry is made consisting of TF and the efficiency. This is accomplished by the PRINT statement labeled LAST. In this case the program will not return to START but will automatically return to the THROUGH LAST statement where TF will be incremented by an amount DELT.

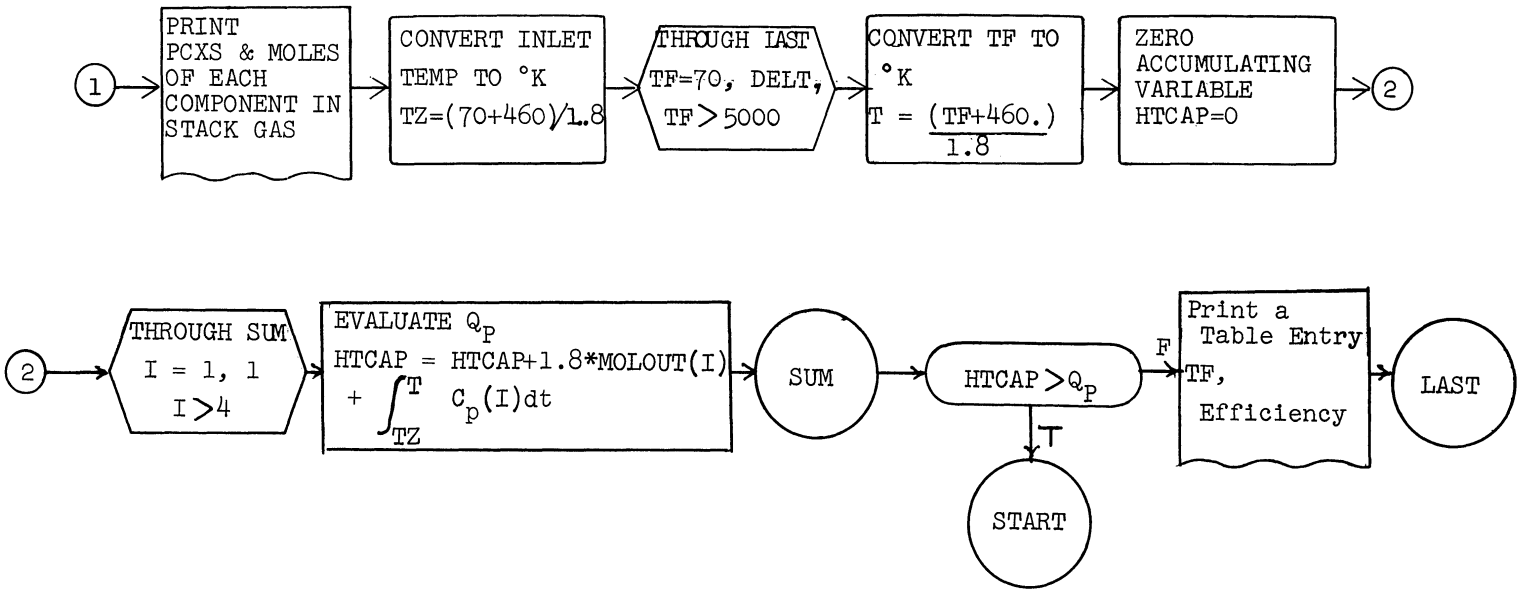
The statements which follow the statement labeled LAST are merely the VECTOR VALUES statements which preset the formats for input and output statements, i.e. READ and PRINT statements, in the executable part of the program.

The data cards for the program follow the $DATA card. In this case, two tables will be prepared, one with PCXS = 20% and DELT=200°F, and the other with PCXS = 10% and DELT=100°F.

Flow Diagram



Flow Diagram (continued)



MAD Program and Data

```
 BRICE CARNAHAN                  S225C                 001    010    000       FURNACE
 BRICE CARNAHAN                  S225C                 001    010    000       FURNACE
$COMPILE MAD, PRINT OBJECT, EXECUTE, DUMP                                      FURN 001
          R
          R FURNACE EFFICIENCY AS A FUNCTION OF STACK GAS TEMPERATURE
          R
           DIMENSION MOLOUT(4)
           INTEGER PCXS, I
           VECTOR VALUES A(1) =  8.27, 6.50, 8.22, 10.34
           VECTOR VALUES B(1) =  .000258, .001, .00015, .000274
           VECTOR VALUES C(1) = 0.0, 0.0, .0000 134, 0.0
           VECTOR VALUES D(1) = -187700., 0.0,  .0, -195500.
          R
          R THE EXECUTABLE PART OF THE PROGRAM BEGINS HERE
          R
START      READ FORMAT INPUT, PCXS, DELT
           MOLOUT(1) = 2.*(PCXS/100.)
           MOLOUT(2) = 2.*(100 + PCXS)*(79./21.)/100.
           MOLOUT(3) = 0.017*2.0*(100 + PCXS)*29./(18.*100.) + 2.
           MOLOUT(4) = 1.0
           PRINT FORMAT HEDING,PCXS, 0.0, MOLOUT(1)...MOLOUT(4)
           TZ = 530./1.8
           THROUGH LAST, FOR TF= 70.,DELT,TF.G.5000.
           T = (TF+460.)/1.8
           HTCAP = 0.
           THROUGH SUM, FOR I = 1, 1, I.G.4
SUM        HTCAP = HTCAP + ( A(I)*(T-TZ ) + B(I)*(T.P.2-TZ.P.2)/2. +
          1C(I)*(T.P.3- TZ.P.3)/3. +D(I)*(1./TZ - 1./T))*1.8*MOLOUT(I)
           WHENEVER HTCAP .G. 344032., TRANSFER TO START
LAST       PRINT FORMAT RESULT , TF, (344032. - HTCAP)/344032.*100.
          R
          R FORMATS FOR THE READ AND PRINT STATEMENTS
          R
           VECTOR VALUES INPUT = $I5,F10.4*$
           VECTOR VALUES HEDING = $22H1PERCENT EXCESS AIR =  I4/45HOSTAC
          1K GAS COMP. FOR ONE MOLE METHANE IN FEED  /30H0MOLES OF METHA
          2NE           =  F6.4/30H MOLES OF OXYGEN             =  F6.4/
          330H MOLES OF NITROGEN          =  F6.4/ 30H MOLES OF WATER VA
          4POR       =  F6.4/30H MOLES OF CARBON DIOXIDE    =  F6.4/
          5     9H4TEMP.(F) S5,  15HPCT. EFFICIENCY    //*$
           VECTOR VALUES RESULT = $1H F8.1, F16.1*$
END        END OF PROGRAM
$DATA
   20   200.
   10   100.
```

Computer Output

The computer output has been modified slightly to conserve space.

Output for First Data Card

PERCENT EXCESS AIR = 20

STACK GAS COMP. FOR ONE MOLE METHANE IN FEED

MOLES OF METHANE	= 0.0000
MOLES OF OXYGEN	= 0.4000
MOLES OF NITROGEN	= 9.0286
MOLES OF WATER VAPOR	= 2.0657
MOLES OF CARBON DIOXIDE	= 1.0000

TEMP.(F)	PCT. EFFICIENCY
70.0	100.0
270.0	94.7
470.0	89.3
670.0	83.8
870.0	78.2
1070.0	72.5
1270.0	66.6
1470.0	60.7
1670.0	54.7
1870.0	48.6
2070.0	42.3
2270.0	36.0
2470.0	29.5
2670.0	22.9
2870.0	16.2
3070.0	9.3
3270.0	2.4

Output for Second Data Card

PERCENT EXCESS AIR = 10

STACK GAS COMP. FOR ONE MOLE METHANE IN FEED

MOLES OF METHANE	= 0.0000
MOLES OF OXYGEN	= 0.2000
MOLES OF NITROGEN	= 8.2762
MOLES OF WATER VAPOR	= 2.0603
MOLES OF CARBON DIOXIDE	= 1.0000

TEMP.(F)	PCT. EFFICIENCY
70.0	100.0
170.0	97.6
270.0	95.1
370.0	92.6
470.0	90.1
570.0	87.5
670.0	85.0
770.0	82.4
870.0	79.8
970.0	77.1
1070.0	74.5
1170.0	71.8
1270.0	69.1
1370.0	66.3
1470.0	63.6
1570.0	60.8
1670.0	58.0
1770.0	55.2
1870.0	52.3
1970.0	49.4
2070.0	46.5
2170.0	43.6
2270.0	40.6
2370.0	37.6
2470.0	34.6
2570.0	31.5
2670.0	28.5
2770.0	25.3
2870.0	22.2
2970.0	19.0
3070.0	15.8
3170.0	12.6
3270.0	9.3
3370.0	6.0
3470.0	2.7

Discussion of Results

The printed output from the program is shown for two different sets of input parameters. The first solution is for the case of 20% excess air and a 200F° temperature interval in the table, i.e. the solution for the originally stated problem. The second set is for 10% excess air and a 100F° table increment, and illustrates that with an almost trivial increase in complexity (reading PCXS and DELT from data cards rather than incorporating them as constants into the body of the program) a computer program can be generalized to solve a more general class of problems of which the one at hand is simply a specific case.

Note also that since the adiabatic flame temperature of the combustion gases is simply the temperature at which the furnace efficiency equals zero, this simple program with three or four additional statements could calculate the flame temperature of any mixture of air and methane as long as the original built-in assumptions (complete combustion, 50% relative humidity etc.) were satisfied. These restrictions could of course be removed also if additional generalization were introduced.

Example Problem No. 89

MASS OR HEAT TRANSFER BY DIFFUSION

by

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Course: Physical Metallurgy Credit hours: 4 Level: Junior or Senior

Statement of Problem

Iron at elevated temperatures and in a CO atmosphere will dissolve carbon interstitially to produce a carbon gradient in the iron. The gradient produced is a function of time, and the diffusion equation relating concentrations, time and the diffusion constant is as follows:

$$(C - CO)/(C1-CO) = 1 - \mathrm{erf}(X/2(Dt)^{0.5})$$

where

C = Concentration of carbon at depth X

CO = Initial carbon concentration in the iron

C1 = Carbon concentration at the surface of the iron

D = Diffusion constant

t = Diffusion time

erf = error function

A library subroutine is available in The University of Michigan Executive System to calculate erf(x) for a given value of x. For problems where the error function is not used directly as such, but which requires the "inverse error function," (i.e., the inverse error function, $x = \mathrm{erf}^{-1}(y)$, is defined herein to mean the value, x, for which erf(x) = y) a more involved system of programming is required in order to obtain solutions. The problem given here is of this type.

The following are experimental data of carbon concentration versus depth below the surface of an iron sample that was carburized for 10 hours at a temperature of 1700°F. The initial carbon concentration in the iron was 0.0%, while the surface carbon potential is 1.30%.

Distance Below Surface, Cm	Carbon Conc. Per cent
0.025	1.00
0.050	0.80
0.075	0.59
0.100	0.42
0.125	0.30
0.150	0.20
0.175	0.14
0.200	0.10
0.225	0.08
0.250	0.03
0.275	0.01

Evaluate the diffusion coefficient, D, from the above data.

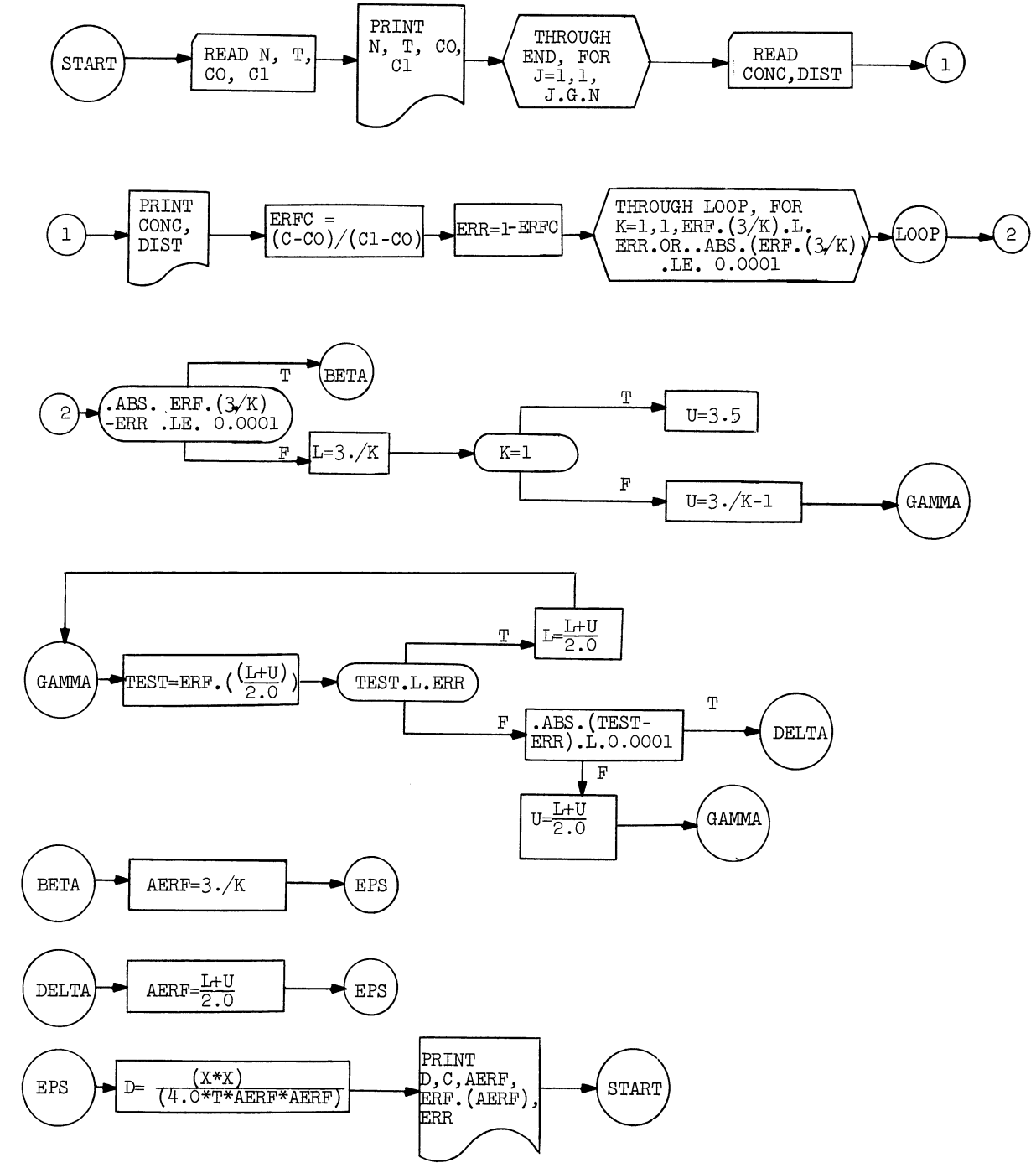
Solution

The method of solution is self explanatory from the flow diagram, MAD program, and computer output which follow.

Since there is no subroutine to generate the inverse error function the program is written in such a fashion that a value is assumed for the error function, the argument calculated, then compared with the value being sought, until the assumed value yields an argument which agrees with the argument being sought to as close an approximation as is desired.

The flow diagram, program and computer output is as follows:

Flow Diagram



MAD Program

```
START   READ FORMAT INPUT, N, T, CO, C1
        VECTOR VALUES INPUT = $ I5, E10.3, 2F10.5*$
        PRINT FORMAT OUT, N, T, CO, C1
        VECTOR VALUES OUT = $1HO, 13HDATA POINTS = I5, S5, 6HTIME = E
       110.3, S5, 20HBASE CONCENTRATION = F10.5, S5, 23HSURFACE CONCE
       2NTRATION = F10.5*$
        THROUGH END, FOR J =1,1, J.G.N
        READ FORMAT DATA, C, X
        VECTOR VALUES DATA = $ 2F10.5*$
        PRINT FORMAT CRIG, C, X
        VECTOR VALUES ORIG =$1HO, S10, 15HCONCENTRATION = F10.5, S10,
       31OHDISTANCE = F10.5*$
        INTEGER J ,N ,K
        ERFC = (C-CO)/(C1-CO)
        ERR = 1.0 - ERFC
LOOP    THROUGH LOOP, FOR K= 1,1, ERF.(3.0/K).L. ERR.OR..ABS.(ERF.(3.
       10/K)- ERR) .LE. 0.0001
        WHENEVER .ABS.(ERF.(3.0/K) -ERR).LE.0.0001, TRANSFER TO BETA
        L = 3.0/K
        WHENEVER K.E.1
        U=3.5
        OTHERWISE
        U = 3.0/(K-1)
        END OF CONDITIONAL
GAMMA   TEST = ERF.((L+U)/2.0)
        WHENEVER TEST .L. ERR
        L = (L+U)/2.0
        TRANSFER TO GAMMA
        OTHERWISE
        WHENEVER .ABS.(TEST -ERR) .L. 0.0001, TRANSFER TO DELTA
        U = (L+U)/2.0
        TRANSFER TO GAMMA
        END OF CONDITIONAL
BETA    AERF = 3.0/K
        TRANSFER TO EPS
DELTA   AERF = (L+U)/2.0
EPS     D = X*X/(4.0*T*AERF*AERF)
END     PRINT FORMAT OUTPUT, D, C, X, AERF, ERF.(AERF), ERR
        VECTOR VALUES OUTPUT =$1H , 3HD = E10.3, S3, 6HCONC = F10.5,
       4S3, 6HDIST = F10.5, S3, 6HAERF = F10.5, S3, 12HERF.(AERF) = F
       510.5, S3, 5HERR = F10.5*$
        TRANSFER TO START
        END OF PROGRAM
```

Computer Output

DATA POINTS = 11 TIME =.360E 05 BASE CONCENTRATION =.00000 SURFACE CONCENTRATION = 1.300

	CONCENTRATION = 1.00000		DISTANCE = .02500					
D = .101E-06	CONC = 1.00000	DIST =	.02500	AERF =	.20748	ERF.(AERF) =	.23080	ERR = .23077
	CONCENTRATION = .80000		DISTANCE = .05000					
D = .138E-06	CONC = .80000	DIST =	.05000	AERF =	.35531	ERF.(AERF) =	.38467	ERR = .38462
	CONCENTRATION = .59000		DISTANCE = .07500					
D = .139E-06	CONC = .59000	DIST =	.07500	AERF =	.52969	ERF.(AERF) =	.54620	ERR = .54615
	CONCENTRATION = .42000		DISTANCE = .10000					
D = .142E-06	CONC = .42000	DIST =	.10000	AERF =	.69880	ERF.(AERF) =	.67697	ERR = .67692
	CONCENTRATION = .30000		DISTANCE = .12500					
D = .151E-06	CONC = .30000	DIST =	.12500	AERF =	.84741	ERF.(AERF) =	.76925	ERR = .76923
	CONCENTRATION = .20000		DISTANCE = .15000					
D = .154E-06	CONC = .20000	DIST =	.15000	AERF =	1.00854	ERF.(AERF) =	.84622	ERR = .84615
	CONCENTRATION = .14000		DISTANCE = .17500					
D = .164E-06	CONC = .14000	DIST =	.17500	AERF =	1.13770	ERF.(AERF) =	.89237	ERR = .89231
	CONCENTRATION = .10000		DISTANCE = .20000					
D = .178E-06	CONC = .10000	DIST =	.20000	AERF =	1.25098	ERF.(AERF) =	.92313	ERR = .92308
	CONCENTRATION = .08000		DISTANCE = .22500					
D = .201E-06	CONC = .08000	DIST =	.22500	AERF =	1.32227	ERF.(AERF) =	.93851	ERR = .93846
	CONCENTRATION = .03000		DISTANCE = .25000					
D = .168E-06	CONC = .03000	DIST =	.25000	AERF =	1.60693	ERF.(AERF) =	.97695	ERR = .97692
	CONCENTRATION = .01000		DISTANCE = .27500					
D = .146E-06	CONC = .01000	DIST =	.27500	AERF =	1.88672	ERF.(AERF) =	.99237	ERR = .99231

Discussion of Results

The results obtained above required 0.70 minutes of IBM 704 computer time for compilation of the MAD program and 0.40 minutes for execution. By contrast, the identical program required 0.32 minutes for compilation on the IBM 709 and 0.58 minutes for execution.

This same program can be used to solve unsteady-state heat transfer problems. In place of C, CO, and C1 where these are concentrations in the diffusion problem, one can use temperatures. For the diffusion constant, one can use the thermal diffusivity.

Example Problem No. 90

PREDICTING THE SCRAP REQUIREMENT FOR THE OXYGEN STEEL CONVERTING PROCESS

by

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Course: Metallurgical Process Design Credit hours: 4 Level: Senior

Statement of Problem

The computer analysis of oxygen steel converting has recently become operational at a Pennsylvania plant of one of the larger steel companies. The program considers 13 variables which include hot metal analysis, temperature, oxygen flow rate, process geometries, and several others which influence the control of the converting process. The commercial computer program is highly empirical, and although of limited accuracy, it has produced marked improvement in control of the operation.

In an effort to illustrate the magnitude of the process, and some of the thermochemical interactions which play a role in design and operation of oxygen converters, a problem was selected for computer analysis which requires a mass and thermal balance for the oxygen steelmaking process. The relationship selected for investigation is the influence of silicon content of the hot metal on the required scrap addition. Computation of the mass balance involves a trial-and-error calculation, and the thermal balance requires lengthy calculations of the heat effect of each reaction, a task suitable for the digital computer.

Write and test a MAD Program which will permit a calculation of the scrap requirement for an oxygen-steelmaking converter, and use the program to determine the influence of silicon content of the hot metal on scrap consumption.

The following assumptions may be made.

Heat losses are 2×10^6 BTU/hr

Production rate is 80 tons/hr

Flue dust losses are 3% of hot metal charged and exit at hot metal charging temperature.

Use the following data to test your program.

	%Si	%Mn	%C	%P	Temperature
Hot metal	0.5-2.0	1.30	4.40	0.13	2500°F
Blown metal	0.02	0.20	0.05	0.02	3000°F
Scrap	Same as Blown metal				77°F
Oxygen	99.5% oxygen				77°F
Burnt lime	Available CaO = 92%				77°F
Mill Scale	(0.15 lb/lb-burnt-lime) 50% FeO				77°F
Slag	Basicity ratio ($\%CaO/\%SiO_2$) = 3.0				3000°F
Combustion gas	100% CO				3000°F

The following thermodynamic data may be used.

1. Heats of Reaction at 77°F

	ΔH, BTU/lb-mole
$P_2(g) + 3\ CaO + 5/2\ O_2(g) \longrightarrow Ca_3P_2O_8$	-1,016,000
$2\ Fe + 3/2\ O_2(g) \longrightarrow Fe_2O_3$	-354,000
$Fe + 1/2\ O_2 \longrightarrow FeO$	-114,800
$Si + O_2(g) \longrightarrow SiO_2$	-369,700
$Mn + 1/2\ O_2(g) \longrightarrow MnO$	-165,600
$2CaO + SiO_2 \longrightarrow 2CaO \cdot SiO_2$	-53,640
$FeO + SiO_2 \longrightarrow FeSiO_3$	-8,100
$MnO + SiO_2 \longrightarrow MnSiO_3$	-10,600
$C(gr) + 1/2\ O_2(g) \longrightarrow CO(g)$	-26,416
$C(gr) + O_2(g) \longrightarrow CO_2(g)$	-94,052

2. Heats of Solution, BTU/lb-mole T in °F.

$Si_{77°F} \longrightarrow \underline{Si}_T$	$\Delta H = 6.7\ T - 34,150$
$Mn_{77°F} \longrightarrow \underline{Mn}_T$	$\Delta H = 11.0\ T + 2,900$
$1/2\ P_2(g)_{77°F} \longrightarrow \underline{P}_T$	$\Delta H = 4.45\ T - 92,500$
$C(gr)_{77°F} \longrightarrow \underline{C}_T$	$\Delta H = 5.23\ T + 10,020$

3. Sensible Heats - Reference Temperature 77°F, T in °F.

Iron-Base Metal (liquid)	$\Delta H = 0.184\ T + 63$ BTU/lb.
Slag (liquid)	$\Delta H = 875 + (T - 2820) \times 0.3$ BTU/lb.
CO	$\Delta H = 23,200 + (T - 3000) \times 8.5$ BTU/lb-mole
CO_2	$\Delta H = 37,400 + (T - 3000) \times 14.4$ BTU/lb-mole
N_2	$\Delta H = 23,000 + (T - 3000) \times 8.6$ BTU/lb-mole

Solution

The diagramming of a sequence to solve this problem requires a relatively complete understanding of the steelmaking process. The oxygen converting process for producing steel had been discussed in detail in class prior to presenting this problem, which is a detailed examination of the process in terms of its mass and energy requirements, and involves a complete examination of one of the principal process variables.

The solution requires that a mass balance be completed which satisfies the production rate to which the heat losses are tied. Upon completion of the mass balance, the excess heat energy is calculated to determine the amount of scrap which is required to maintain the process temperature below its thermal limit. This scrap plus the refined steel produced by oxidizing the impurities from the blast furnace hot metal charged to the converter must satisfy the production specified.

The mass balance involves a trial and error computation since the burnt lime added depends upon the silicon which is oxidized from the hot metal, and the basicity ratio of the slag. Mill scale, added to supply additional oxygen to the process, is defined in terms of the lime added. The thread which runs through the several input and output streams of the converting process is the requirement that the charged iron, a constituent of all of the condensed phase streams (i.e., all except the oxygen lanced into the converter and the combustion gases exiting from the process) must be equal to the iron removed. The mass balance is then defined in terms of an iron balance.

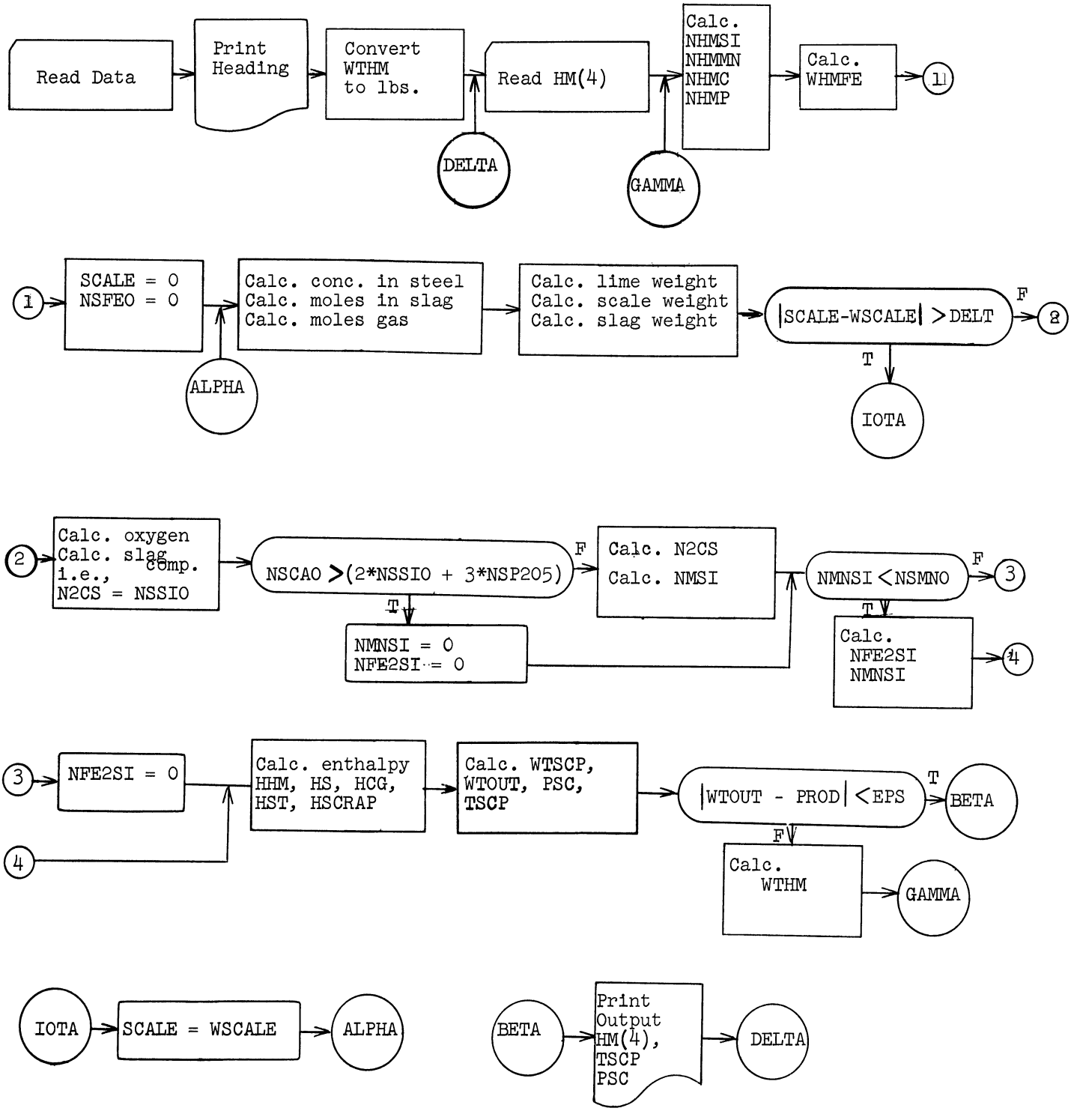
The method of calculation is as follows.

1. Calculate the moles of silicon, manganese, carbon, and phosphorous in the hot metal which is assumed to be charged, correcting its value for any flue-dust losses.
2. Initialize the weight of scale added, and the moles of iron in the slag stream at zero.
3. Correct the value for the weight of iron in the hot metal by adding the weight of iron in the scale and subtracting the weight of iron in the slag.
4. Calculate the weight of refined steel produced from the hot metal charged on the basis of an iron balance.
5. Calculate the moles of silicon, manganese, carbon, and phosphorous which remain in the steel, subtracting them from the results of step 1 to determine the moles which enter the slag stream.
6. Calculate the mole fraction of iron oxide in the slag using a relationship involving the carbon content of the finished steel.
7. Calculate the weight of burnt lime added to provide the correct basicity ratio in the slag, assuming silica to be the only acidic slag component.
8. Calculate the weight of scale added on the basis of the result of step 7, and calculate the weight of slag produced.
9. Compare the weight of scale calculated with that used in step 3. If they agree within a limit of error continue on; otherwise, return to step 3, substituting the result of step 8.
10. Calculate the composition of the slag in terms of the compounds which form, assuming a preferred order to the reactions.
11. Compute the enthalpy of each of the streams, the hot metal charged, the slag, combustion gases, and steel produced. The inlet enthalpy of the hot metal (including the oxidizing reactions which occur) minus the enthalpy of the slag, combustion gases, steel, and heat lost from the vessel will yield the excess energy which is available to melt scrap.

12. Calculate the scrap which can be melted, and the metal produced which is the scrap plus the refined steel.

13. Compare the metal produced with that associated with the reported heat loss. If they do not agree, correct the assumed hot metal charge proportionately and return to step 1.

Flow Diagram



List of Variables

HM(1)...HM(3)	Linear array for storage of the words, "hot metal"
HM(4)	Weight percent silicon in the hot metal
HM(5)	Weight percent manganese in the hot metal
HM(6)	Weight percent carbon in the hot metal
HM(7)	Weight percent phosphorus in the hot metal
HM(8)	Temperature of the hot metal in ^{o}F
SCRAP(1)...SCRAP(3)	Linear array for storage of the word, "scrap"
SCRAP(4)	Weight percent silicon in the scrap
SCRAP(5)	Weight percent manganese in the scrap
SCRAP(6)	Weight percent carbon in the scrap
SCRAP(7)	Weight percent phosphorus in the scrap
SCRAP(8)	Temperature of the scrap in ^{o}F
STEEL(1)...STEEL(3)	Linear array for storage of the word, "steel"
STEEL(4)	Weight percent silicon in the steel
STEEL(5)	Weight percent manganese in the steel
STEEL(6)	Weight percent carbon in the steel
STEEL(7)	Weight percent phosphorus in the steel
STEEL(8)	Finishing temperature of the steel in ^{o}F
POXYO2	Percent oxygen in the oxygen stream
A	Available base in the lime flux
PSCFEO	Weight percent FeO in the scale
RCO2	CO2/CO ratio in the stack gas
TO2	Temperature of the oxygen in ^{o}F
TSC	Temperature of the scrap in ^{o}F
TS	Temperature of the slag at tap in ^{o}F
TCG	Average temperature of the combustion gas in ^{o}F
HL	Heat loss in BTU's per hour
PROD	Production in lbs. per heat
FDLOSS	Flue dust lost as percent of hot metal weight charged
WTHM	Estimated weight of hot metal to be charged in tons
DELT	Allowable error in calculated scale weight
EPS	Allowable error in calculated production
BR	Basicity ratio, moles CaO/moles SiO2
WTHM	Weight of hot metal, converted to lbs. in computer program
NHMSI	Moles of silicon in hot metal
NHMMN	Moles of manganese in hot metal
NHMC	Moles of carbon in hot metal
NHMP	Moles of phosphorus in hot metal
WHMFE	Lbs. of iron in hot metal charged
SCALE	Weight of scale
NSFEO	Moles of FeO in slag
WST	Weight of steel in lbs.
NSTSI	Moles of silicon in steel
NSTMN	Moles of manganese in steel
NSTC	Moles of carbon in steel
NSTP	Moles of phosphorus in steel

List of Variables, Continued

NSSIO	Moles of silica in slag
NSMNO	Moles of MnO in slag
NSP2O5	Moles of P2O5 in slag
NCCG	Moles of carbon in combustion gas
XSFEO	Mole fraction of FeO in slag
NSCAO	Moles of lime in slag
WTLIME	Weight of lime charged in lbs.
WSCALE	Weight of scale charged in lbs.
WTSLAG	Weight of slag in lbs.
NOXYO	Moles of O supplied by oxygen stream
SCFOX	Standard cubic feet of oxygen required for heat
N2CS	Moles of 2CaO.SiO2 in slag
NMNSI	Moles of MnO.SiO2 in slag
NFE2SI	Moles of 2FeO.SiO2 in slag
HHM	Enthalpy of charged hot metal
HS	Enthalpy of finishing slag
HCG	Enthalpy of combustion gases
HST	Enthalpy of finishing steel
HSCRAP	Heat available for melting scrap
WTSCP	Weight of scrap to be charged
WTOUT	Lbs. of steel produced
PSC	Percent scrap to be charged
TSCP	Tons of scrap to be charged

MAD Program and Data

```
 R. D. PEHLKE                    C07-N              0 3   030   000      CHE 13
 R. D. PEHLKE                    C07-N              0 3   030   000      CHE 13
$COMPILE MAD, PRINT OBJECT, EXECUTE, DUMP
          DIMENSION HM(10), STEEL(10), SCRAP(10)
          READ FORMAT INPUT1, HM(1)...HM(8), STEEL(1)...STEEL(8),
         2SCRAP(1)...SCRAP(8)
          VECTOR VALUES INPUT1 = $(3C6,4F6.3,F6.0)*$
          READ FORMAT INPUT2, POXYO2, A, PSCFEO,BR,RCO2,TO2,TSC,TS,TCG
          VECTOR VALUES INPUT2 = $5F8.4,4F5.0*$
          READ FORMAT INPUT3, HL,PROD,FDLOSS,WTHM
          VECTOR VALUES INPUT3 = $4F15.4*$
          READ  FORMAT INPUT4,DELT,EPS
          VECTOR VALUES INPUT4 = $2F10.4*$
          PRINT FORMAT TITLE
          VECTOR VALUES TITLE = $1H1,65H INFLUENCE OF SILICON ON SCRAP
         2ADDITION TO BASIC OXYGEN CONVERTER  ////*$
          PRINT FORMAT DATA1,HM(1)...HM(8), STEEL(1)...STEEL(8),
         2SCRAP(1)...SCRAP(8)
          VECTOR VALUES DATA1= $5H DATA//S14,31H COMPOSITIONS IN WEIGHT
         2 PERCENT/S19,3H SI,S4,5H MN,S4,2H C,S4,2H P,S3,5H TEMP//(3C6,
         34F6.3,F6.0)//*$
          PRINT FORMAT DATA2, POXYO2, A, PSCFEO, RCO2, TO2, TSC, TS,
         2TCG, HL, PROD, FDLOSS, WTHM, DELT, EPS, BR
          VECTOR VALUES DATA2 = $26H PERCENT OXYGEN IN BLAST =F6.2/33H
         2PERCENT AVAILABLE BASE IN LIME =F6.2/23H PERCENT FEO IN SCALE
         3 =F6.2/33H CO2/CO RATIO IN COMBUSTION GAS =F6.2/24H TEMPERATU
         4RE OF OXYGEN =F6.0/23H TEMPERATURE OF SCRAP =F6.0/22H TEMPERA
         5TURE OF SLAG =F6.0/32H TEMPERATURE OF COMBUSTION GAS =F6.0/
         620H HEAT LOSS, BTU/HR =F8.0/21H PRODUCTION, LBS/HR =F7.0 /35H
         7 FLUE DUST LOSS, PCT OF HOT METAL =F6.2/43H WEIGHT OF HOT MET
         8AL TO START TRIAL, TONS =F6.0/44H ALLOWABLE ERROR IN SCALE WE
         9IGHT, DELT, LB =F6.0/50H ALLOWABLE ERROR IN WEIGHT OF METAL O
         1UT, EPS, LB =F8.0/25H BASICITY RATIO OF SLAG = F6.4////*$
          PRINT FORMAT HEAD
          VECTOR VALUES HEAD = $S5,20H PCT SI IN HOT METAM,S3,20H PCT S
         2CRAP IN CHARGE,S3,17H TONS SCRAP ADDED//*$
         R  MASS BALANCE
          WTHM = WTHM*2000.
DELTA     READ FORMAT INPUT5, HM(4)
          VECTOR VALUES INPUT5 = $F6.3*$
GAMMA     NHMSI =(100.-FDLOSS)/100.*WTHM*HM(4)/(100.*28.06)
          NHMMN = (100.-FDLOSS)/10 .*WTHM*HM(5)/(10 .*54.94)
          NHMC = (100.-FDLOSS)/100.*WTHM*HM(6)/(100.*12.01)
          NHMP = (100.-FDLOSS)/100.*WTHM*HM(7)/(100.*30.98)
          WHMFE = (100.-FDLOSS)/10 .*WTHM*(100.-HM(4)-HM(5)-HM(6)-HM(7)
         2)/10 .
          SCALE = 0.0
          NSFEO = 0.0
ALPHA     WHMFE = WHMFE+SCALE*PSCFEO*55.85/(100.*71.85)+SCALE*(100.-
         2PSCFEO)/100.-NSFEO*55.85
          WST = 100.*WHMFE/(100.-STEEL(4)-STEEL(5)-STEEL(6)-STEEL(7))
          NSTSI = WST*STEEL(4)/(10 .*28.06)
          NSTMN = WST*STEEL(5)/(10 .*54.94)
          NSTC = WST*STEEL(6)/(100.*12.01)
          NSTP = WST*STEEL(7)/(100.*30.98)
          NSSIO = NHMSI-NSTSI
          NSMNO = NHMMN-NSTMN
          NSP2O5 = (NHMP-NSTP)/2.
          NCCG = NHMC-NSTC
```

MAD Program and Data (continued)

```
            XSFEO = 0.01/STEEL(6)
            NSCAO = NSSIO*BR
            NSFEO = (NSSIO+NSMNO+NSP2O5+NSCAO)*XSFEO/(1.-XSFEO)
            WTLIME = NSCAO*56.08*100./A
            WSCALE = 0.15*WTLIME
            WTSLAG = NSSIO*60.06+NSMNO*70.94+NSP2O5*141.96+NSFEO*71.85
           2+WTLIME
            WHENEVER.ABS.(SCALE-WSCALE).G.DELT, TRANSFER TO IOTA
            NOXYO = NSSIO*2.+NSMNO+NSP2O5*5.+NSFEO+NCCG*(1.+2.*RCO2)/(1.+
           2RCO2)-WSCALE*PSCFEO*16./(71.85*100.)
            SCFOX = (NOXYO/2.)*379.*100./POXYO2
            N2CS = NSSIO
            WHENEVER NSCAO.G.(2.*NSSIO+3.*NSP2O5)
            NMNSI = 0.0
            NFE2SI = 0.0
            OTHERWISE
            N2CS = (NSCAO-3.*NSP2O5)/2.
            NMNSI = NSSIO-N2CS
            WHENEVER NMNSI.G.NSMNO
            NFE2SI = NSSIO-N2CS-NSMNO
            NMNSI = NSMNO
            OTHERWISE
            NFE2SI = 0.0
            END OF CONDITIONAL
            END OF CONDITIONAL
           R HEAT BALANCE
            HHM =(0.184*HM(8)+63.)*WTHM*(100.-FDLOSS)/100.+(6.7*HM(8)
           2-34150.)*NSSIO+(11.*HM(8)+2900.)*NSMNO+(4.45*HM(8)-92500.)*
           3NSP2O5*2.+(5.23*HM(8)+10 20.)*NCCG
            HS = (875.+(TS-2820.)*0.3)*WTSLAG-1016000.*NSP2O5-53640.*
           2NSSIO-114800.*(NSFEO-WSCALE*PSCFEO/(100.*71.85))-369700.*
           3NSSIO-165600.*NSMNO-5364 .*N2CS-10600.*NMNSI-8100.*NFE2SI
            HCG = (23200.+(TCG-3000.)*8.5-26416.)*NCCG*(1./(1.+RCO2))+ (
           23740 .+(TCG-3000.)*14.4-94052.)*NCCG*(RCO2/1.+RCO2)
            HST = (0.184*TS+63.)*WST
            HSCRAP = HHM-HST-HS-HCG-HL
            WTSCP = HSCRAP/(0.184*(STEEL(8)-TSC)+63.+14.168)
            WTOUT = WST+WTSCP
            PSC = 100.*(WTSCP/(WTSCP WTHM))
            TSCP = WTSCP/2000.
            WHENEVER.ABS.(WTOUT-PROD).L.EPS,TRANSFER TO BETA
            WTHM = WTHM*PROD/WTOUT
            TRANSFER TO GAMMA
BETA        PRINT FORMAT OUTPUT, HM(4), PSC, TSCP
            VECTOR VALUES OUTPUT = $F16.2,F24.2,F22.2*$
            TRANSFER TO DELTA
IOTA        SCALE = WSCALE
            TRANSFER TO ALPHA
            END OF PROGRAM
$DATA
 HOT METAL              500  1300  440     130  2500
 STEEL                   20   200   05      20  3000
 SCRAP                   20   200   05      20    77
  995     92000   500000   3                  77   77 3     3000
    2000000          160000                  3                60
    100     1000
   000
   200
   400
   600
   800
  1000
  1200
  1400
  1600
  1800
  2000
```

Computer Output

INFLUENCE OF SILICON ON SCRAP ADDITION TO BASIC OXYGEN CONVERTER

DATA

	COMPOSITIONS IN WEIGHT PERCENT SI	MN	C	P	TEMP
HOT METAL	.500	1.300	4.40	.130	2500.
STEEL	.020	0.200	0.05	.020	3000.
SCRAP	.020	0.200	0.05	.020	77.

PERCENT OXYGEN IN BLAST = 99.50
PERCENT AVAILABLE BASE IN LIME = 92.00
PERCENT FEO IN SCALE = 50.00
CO2/CO RATIO IN COMBUSTION GAS = 0.00
TEMPERATURE OF OXYGEN = 77.
TEMPERATURE OF SCRAP = 77.
TEMPERATURE OF SLAG = 3000.
TEMPERATURE OF COMBUSTION GAS = 3000.
HEAT LOSS, BTU/HR =2000000.
PRODUCTION, LBS/HR =160000.
FLUE DUST LOSS, PCT OF HOT METAL = 3.00
WEIGHT OF HOT METAL TO START TRIAL, TONS = 60.
ALLOWABLE ERROR IN SCALE WEIGHT, DELT, LB = 10.
ALLOWABLE ERROR IN WEIGHT OF METAL OUT, EPS, LB = 1000.
BASICITY RATIO OF SLAG =3.0000

PCT SI IN HOT METAL	PCT SCRAP IN CHARGE	TONS SCRAP ADDED
0.00	9.31	8.08
0.20	12.09	10.50
0.40	14.55	12.66
0.60	16.89	14.71
0.80	19.10	16.66
1.00	21.19	18.51
1.20	23.18	20.27
1.40	25.07	21.95
1.60	26.87	23.55
1.80	28.59	25.08
2.00	30.22	26.54

Discussion of Results

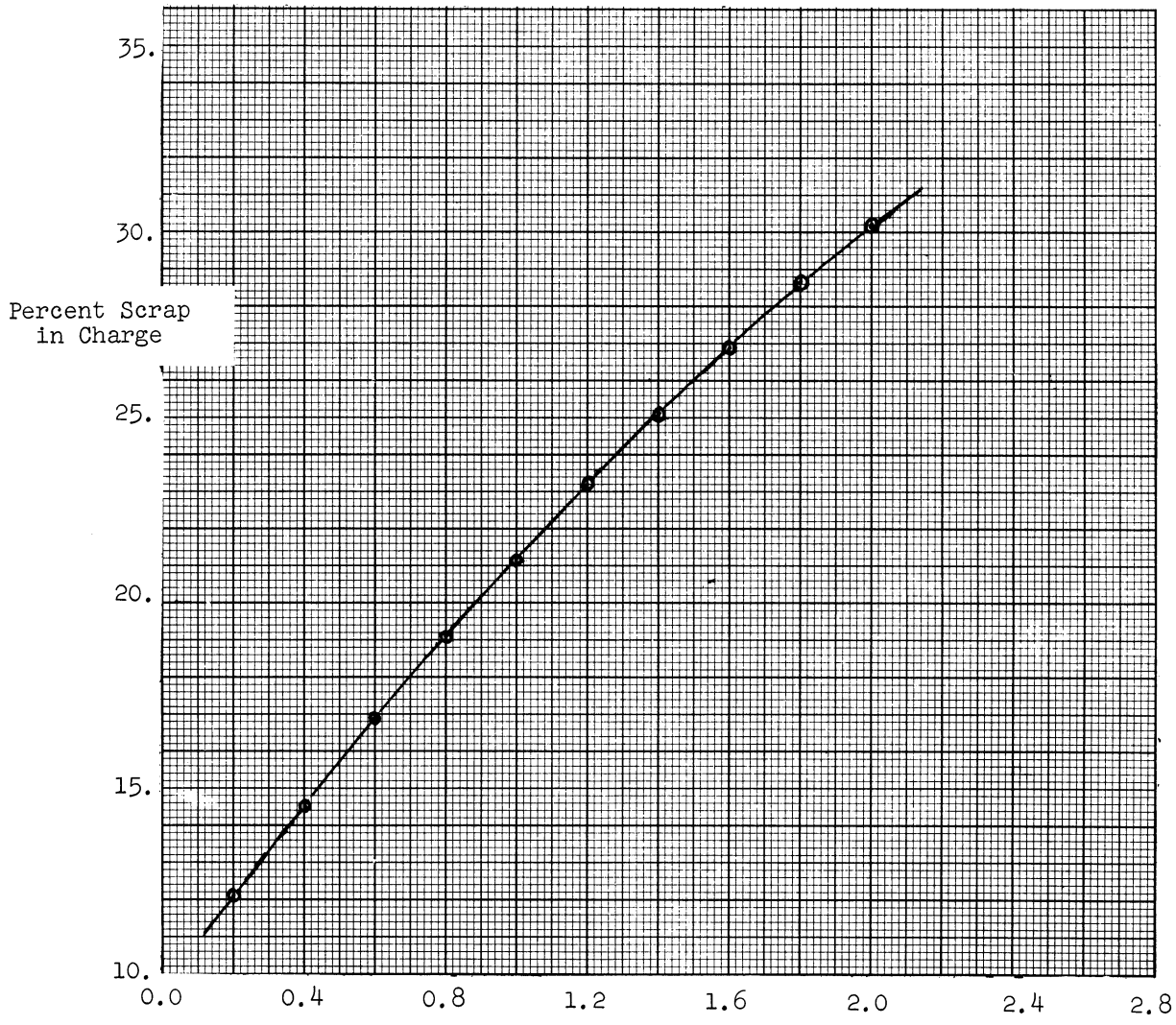
The results printed out by the computer are the percent silicon in the charged hot metal, the percent scrap in the charge which is the calculated scrap divided by the sum of the scrap and the hot metal charged, and the actual number of tons of scrap added to the operation which produces 80 tons per hour in the case under consideration.

As the silicon content of the hot metal increases, the excess heat available for melting scrap increases resulting in a higher scrap percentage in the charge as shown in the figure below.

The structure of the computer program is such that other variables may be investigated, including the influences of changing the temperatures of the process. One commercial proposal for increasing the ability of the process to handle scrap involves preheating the charged scrap,

thus decreasing the heat units required to accomplish melting. This program can be used to study the effect of preheating to various temperature levels. Other compositional variables can also be studied.

Effect of Silicon Content of Hot Metal on Percent Scrap
in Charge of 80 ton/hr Oxygen Converter



Critique

Of the 23 solutions attempted by the class to which this problem was assigned, only three were successful. These three solutions employed essentially the same approach outlined above, and yielded results in reasonable agreement.

Nonetheless, this particular problem is an excellent one for use in the terminal course in extractive metallurgy. The relatively unsuccessful performance of the students may be an indication that the problem is too difficult as a class assignment, and might be better used in its finished form as a supplement to the lecture material.

The problem is pertinent to the material covered in the course and was attacked with enthusiasm by the students. The low success rate may serve as an indication that in long and relatively complex problems, additional assistance in programming, and problem outline may be absolutely essential.

The bulk of the class attempted this problem on the IBM 704 system. Two groups of two attempted the problem on the LGP-30, but were not successful in the alloted time of five weeks. Although the class worked individually on the problem, in the case of the small computer the four students were all taking their first look at a new language, and the grouping was suggested. The interpretive language, ACT III, was used but all of the students experienced considerable difficulty in mastering the programming for the LGP-30. This particular experience is a re-enforcement of the view that the large machine, if available, with its user-oriented language and easy accessibility is by far the most desirable for the user.

Example Problem No. 91

PRECISION LATTICE PARAMETER DETERMINATION FOR A CUBIC MATERIAL

by

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Course: X-Ray Studies of Engineering Materials Credit Hours: 3 Level: Senior

Statement of the Problem

Write a computer program for the precision calculation of the lattice parameter of a known cubic material. The following conditions apply:

A. X-ray diffraction exposures are made in a 114.6 mm. diameter cylindrical Debye-Scherrer camera.

B. Plane indices can be determined from rough measurements made with a plastic scale; however, the lattice parameter calculations should be based on line position measurements made on the optical comparator to a precision of $\pm$ 0.0025 cm.

C. The film measurements should be corrected for shrinkage.

D. The Nelson-Riley extrapolation technique should be used to correct for sample absorption errors. A least-squares fit should be employed in the extrapolation.

E. An estimate should be made of the standard deviation of the parameter.

F. A plot should be generated showing the relationship between the parameter values and the Nelson-Riley factor.

G. Provision should be made for discarding diffraction angles of less than 30°.

H. In the back-reflection region, the α_1, and α_2 doublets should be used where resolved.

Solution

For a detailed discussion of the X-ray relationships and procedures, refer to Klug and Alexander (Reference 1). The computer program for the IBM 709 was written in the MAD language. Variable names used in the MAD program are defined in the body of the discussion which follows. They are capitalized and enclosed in parentheses.

The solution employs the Bragg diffraction equation:

$$\lambda_\alpha = 2d_L \sin \theta_L, \quad \text{where} \quad d_L = \frac{a_o}{\sqrt{h^2 + k^2 + \ell^2}}$$

and the Nelson-Riley factor (NELRI),

$$F_L = \frac{1}{2} \left(\frac{\cos^2 \theta_L}{\sin \theta_L} + \frac{\cos^2 \theta_L}{\theta_L} \right)$$

where: λ_α = wave length of the radiation used (LAM1 or LAM2).

d_L = interplanar spacing between successive atomic planes.

θ_L = angle between the atomic plane and the incident and reflected X-ray beam (THETA(L) in radians; ANGLE(L) in degrees).

a_o = the lattice parameter (side length) of the cubic crystal unit cell (LGOOD).

h,k,ℓ = Miller indices of the diffracting plane; $((h^2+k^2+\ell^2)$ is often referred to as N^2, (NN)).

L = the diffraction line in question (L).

All calculations are made in terms of Angstrom Units, A^o, (10^{-8}cm.).

The Bragg equation can be rearranged as follows:

$$a_L = \frac{\lambda_\alpha \sqrt{h^2 + k^2 + \ell^2}}{2 \sin \theta_L}$$

For a given radiation, λ_α (LAM1 or LAM2), a lattice parameter, a_L (LATPA(L)), can be calculated for each diffraction line, L, which is produced at an angle θ_L (THETA(L)) by a particular set of planes, h, k, ℓ.

In a cylindrical Debye-Scherrer camera, systematic errors in θ values are possible due to film shrinkage during processing, displacement of the sample, and absorption of X-rays by the sample. In addition, there can be random errors occurring during subsequent film measurement. Various methods proposed to correct for such errors are discussed fully in Chapter 8 of Reference 1.

The premise of these methods is that functions of θ exist for which systematic errors in θ vary linearly. The precision of sin θ values increases as θ increases and systematic errors in determination of θ approach zero as θ approaches 90^o. Thus, it is possible to extrapolate parameters calculated at intermediate angles to the value of some function at $\theta = 90^o$, where the error is presumably zero (Reference 5). The function proposed by Nelson and Riley (see Reference 1, pp. 464-467) has been found to be highly linear down to very low values of θ and "for all practical purposes" all diffraction angles can be used in employing it. However, for optimum results Klug and Alexander (Reference 1) do recommend that its use be confined, where possible, to angles between $\theta = 30^o$ and 90^o.

The extrapolation is made by the method of least-squares. An equation of the slope-intercept form

$$a_L = m F_L + a_o$$

relates values of the lattice parameter, a_L (LATPA), and the corresponding Nelson-Riley factors, F_L (NELRI). The intercept of this line at $F_L = 0$ (i.e., $\theta = 90^o$) is a_o (LGOOD), the "true" lattice parameter.

In addition to determining the best straight line through the points, an estimate of random errors can be made by calculating the standard deviation of the points from the line. Useful formulae for these computations are given by Moroney (Reference 2) and are as follows:

$$a_o = \frac{(\Sigma F_L)(\Sigma F_L a_L) - (\Sigma a_L)(\Sigma F_L^2)}{(\Sigma F_L)^2 - Q\,\Sigma F_L^2}$$

$$m = \frac{\Sigma(F_L a_L) - (\Sigma F_L)(\Sigma a_L)/Q}{\Sigma F_L^2 - (\Sigma F_L)^2/Q}$$

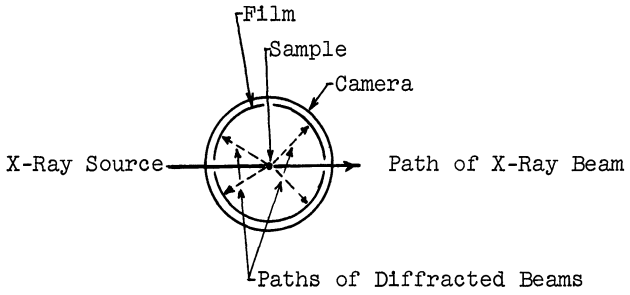
where Σ refers to the summation of the function for all diffraction lines and Q is the total number of lines.

The "standard deviation", σ, is calculated from the equation:

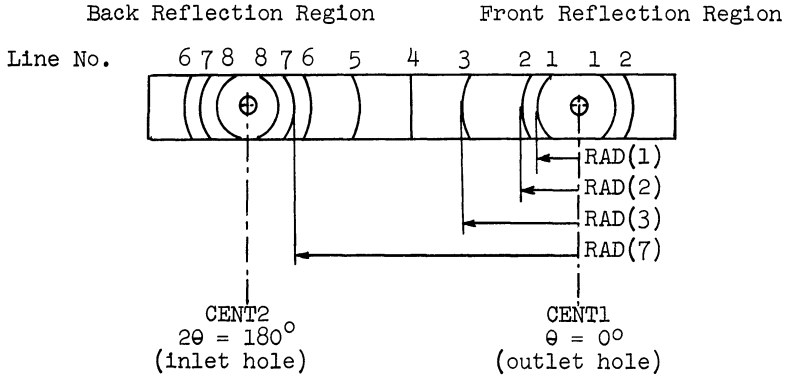
$$\sigma = \sqrt{\frac{\Sigma(mF_L + a_o - a_L)^2}{Q - 1}} \quad ,$$

where the expression $(mF_L + a_o - a_L)$ is the vertical deviation of an individual parameter, a_L, from the least-squares line at F_L.

The film for the X-ray exposure is mounted in the camera as shown below:



Following film development and numbering of the diffraction lines, measurements are made from the strip of film which has the following appearance:



Since the line pairs are not necessarily symmetrical about the inlet and outlet holes, the centers are determined by averaging the distances between corresponding pairs of lines. The geometry of the camera is such that the distances RAD(1), etc. (in millimeters) are approximately equal to twice the diffraction angle (ANGLE). In the process of converting the radius measurements, a shrinkage correction factor is introduced to adjust the results so that the distance CENT1-CENT2 is 90°.

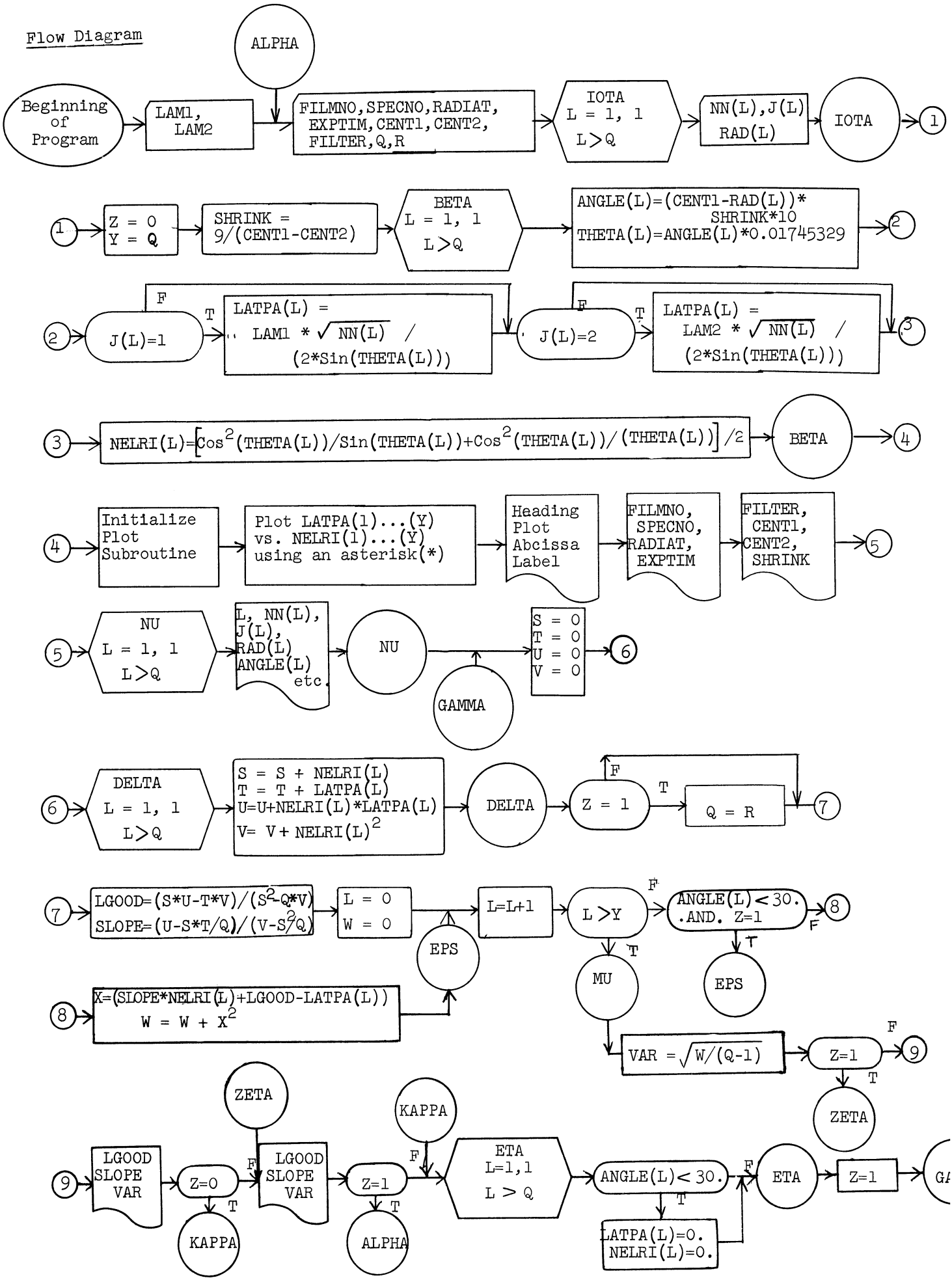
The plane indices are obtained from the ASTM Powder Data File Card for the substance in question. This identification is made from "d" values (see the Bragg equation) which can be determined from readily available charts or tables. A preliminary rough determination of the line positions is made for this purpose.

For the computer run, the wave length of the radiation is known, and the resolution of the α_1(J=1) and α_2(J=2) doublets at high diffraction angles is determined by inspection of the film. The input to the computer consists of the wave length of the radiation (in the example, Cobalt) and an identification card describing the sample and film exposure conditions, and defining the total number of diffraction lines obtained, Q, and the number of lines at $\theta > 30^{\circ}$, R. This is followed by a series of cards, one for each line (L), indicating the line number, the sum of the squares of plane indices (NN), the wave length to be used in the computation (J=1 or 2), and the comparator measurement (RAD(L)). The program then does the following:

1. Computes the shrinkage correction factor (SHRINK).
2. Determines the angle (ANGLE) for each diffraction line, corrects it for shrinkage and converts to radians (THETA).
3. Computes the lattice parameter (LATPA) for each line using the appropriate wave length.
4. Computes the Nelson-Riley factor (NELRI), for each line.
5. Plots the parameter versus the corresponding Nelson-Riley factor.
6. Tabulates the results.
7. Performs a least-squares analysis to determine the extrapolated parameter (LGOOD) and slope (SLOPE) of the least-squares line.
8. Computes the standard deviation (VAR).
9. Repeats steps 7 and 8 for only those angles greater than 30°. (Q is now set equal to R, the number of lines at $\theta > 30^{\circ}$.)
10. Prints a summary of the results from steps 7, 8, and 9.
11. Repeats for the next set of data cards for a new film.

The plot can be used for the elimination of obviously incorrect points by inspection and the program can then be rerun with the corresponding data card or cards eliminated.

Flow Diagram



MAD Program and Data

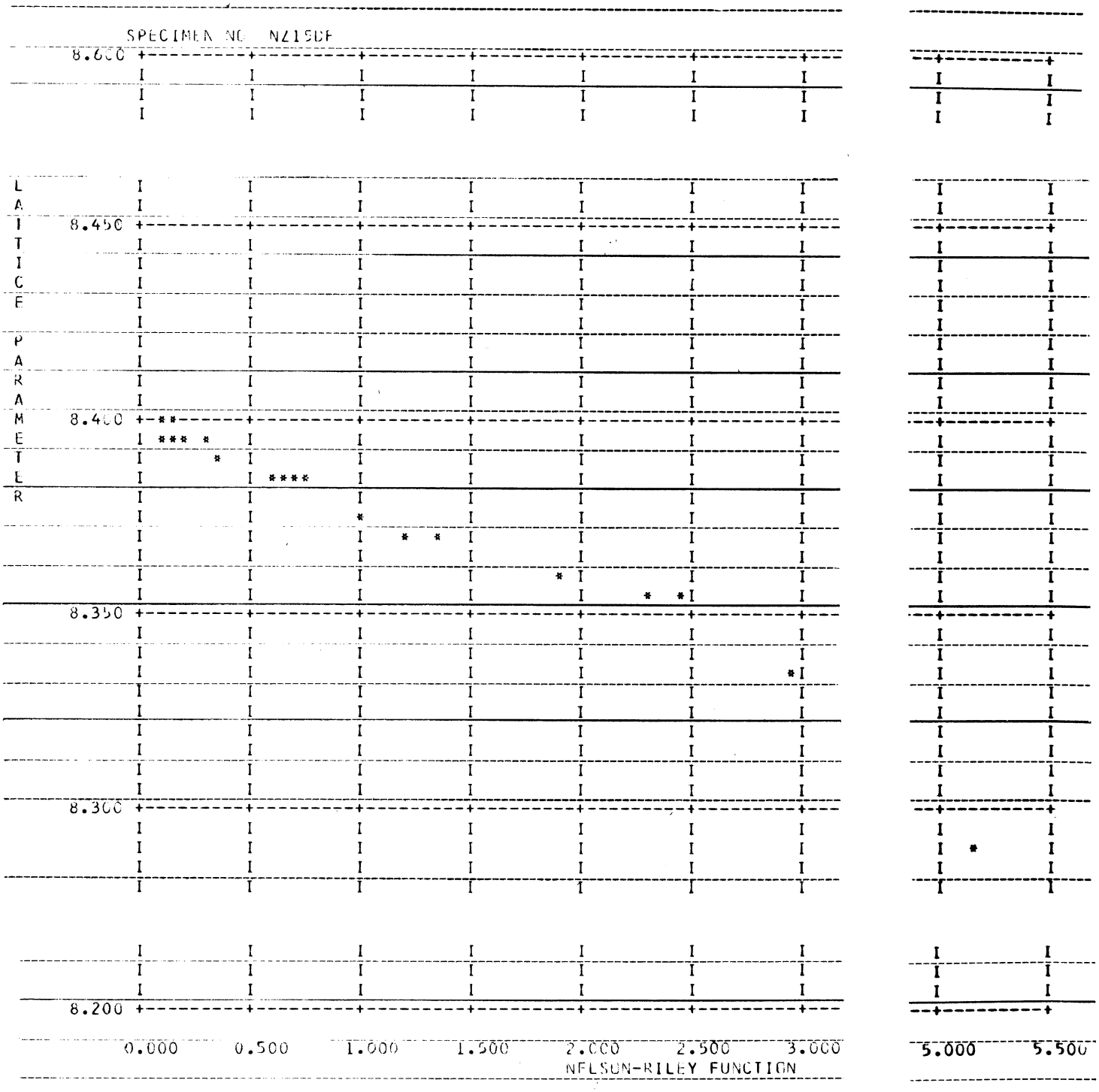
```
 J. V. GLUCK                    S164P              002   020   000
 J. V. GLUCK                    S164P              002   020   000
$COMPILE MAD, EXECUTE, DUMP
          RCALCULATION OF LATTICE PARAMETER
           INTEGER L, Q, SPECNO, RADIAT, FILTER, NN, J, R, Z, FILMNO
          1,Y
           DIMENSION NN(35), RAD(35), THETA(35), LATPA(35), NELRI(35),
          1J(35), ANGLE(35), DUMMY(1539)
           READ DATA
ALPHA      READ FORMAT DATA2, FILMNO, SPECNO, RADIAT, EXPTIM, CENT1,
          1CENT2, FILTER, Q, R
           THROUGH IOTA, FOR L=1,1,L.G.Q
IOTA       READ FORMAT DATA3, NN(L), J(L), RAD(L)
           Z=0
           Y=Q
           SHRINK=9/(CENT1-CENT2)
           THROUGH BETA, FOR L=1,1,L.G.Q
           ANGLE(L)=(CENT1-RAD(L))*SHRINK*10
           THETA(L)=ANGLE(L)*0.01745329
           WHENEVER J(L).E.1, LATPA(L)=(LAM1*SQRT.(NN(L)+0.0))/(2*SIN.(
          1THETA(L)))
           WHENEVER J(L).E.2, LATPA(L)=(LAM2*SQRT.(NN(L)+0.0))/(2*SIN.(
          1THETA(L)))
BETA       NELRI(L)=(COS.(THETA(L)).P.2/SIN.(THETA(L))+COS.(THETA(L)).P.
          12/THETA(L))/2
           EXECUTE PLOT1.(0,8,10,11,10)
           EXECUTE PLOT2.(DUMMY, 5.500,0.,8.600,8.200)
           EXECUTE PLOT3.($*$, NELRI(1), LATPA(1), Y)
           PRINT FORMAT GTITLE, SPECNO
           EXECUTE PLOT4.(45,ORD)
           PRINT FORMAT ABS
           VECTOR VALUES GTITLE=$1H1S9,14H SPECIMEN NO  C6*$
           VECTOR VALUES ORD=$                                LATTICE PARAME
          1TER*$
           VECTOR VALUES ABS=$S50,22H NELSON-RILEY FUNCTION*$
           PRINT FORMAT HEAD, FILMNO, SPECNO, RADIAT, EXPTIM, FILTER,
          1CENT1, CENT2, SHRINK
           THROUGH NU, FOR L=1,1,L.G.Q
NU         PRINT FORMAT ANS1, L, NN(L), J(L), RAD(L), ANGLE(L), LATPA(L)
          1, NELRI(L)
GAMMA      S=0
           T=0
           U=0
           V=0
           THROUGH DELTA, FOR L=1,1,L.G.Q
           S=S+NELRI(L)
           T=T+LATPA(L)
           U=U+NELRI(L)*LATPA(L)
DELTA      V=V+NELRI(L).P.2
           WHENEVER Z.E.1, Q=R
           LGOOD=((S*U)-(T*V))/(S.P.2-(Q*V))
           SLOPE=(U-(S*T/Q))/(V-(S.P.2/Q))
           L=0
           W=0
EPS        L=L+1
           WHENEVER L.G.Y, TRANSFER TO MU
           WHENEVER ANGLE(L).L.30.0 .AND. Z.E.1, TRANSFER TO EPS
           X=(SLOPE*NELRI(L)+LGOOD-LATPA(L))
           W=(W)+(X.P.2)
           TRANSFER TO EPS
```

MAD Program and Data (continued)

```
MU          VAR=SQRT.(W/(Q-1))
            WHENEVER Z.E.1, TRANSFER TO ZETA
            PRINT FORMAT ANS2, LGOOD, SLOPE, VAR
            WHENEVER Z.E.0, TRANSFER TO KAPPA
ZETA        PRINT FORMAT ANS3, LGOOD, SLOPE, VAR
            WHENEVER Z.E.1, TRANSFER TO ALPHA
KAPPA       THROUGH ETA, FOR L=1,1,L.G.Q
            WHENEVER ANGLE(L).L.30.0
            LATPA(L)=0
            NELRI(L)=0
ETA         END OF CONDITIONAL
            Z=1
            TRANSFER TO GAMMA
            VECTOR VALUES HEAD=$1H1S9,9H FILM NO I5,S5,13H SPECIMEN NO C6
           1/S10,12H RADIATION  C4,S3,15H EXPOSURE TIME F3.1,4H HRS/S10,
           1 9H FILTER  C3/S10,10H CENTER 1 F6.3,S3,10H CENTER 2 F6.3,S3,
           116H SHRINK FACTOR= F6.5///S10,59H LINE NO    NN,J     RAD(L)
           1   THETA       LATPA       NELRI*$
            VECTOR VALUES DATA2=$I5, C6, C2, F3.1, 2F6.3, C3, 2I3*$
            VECTOR VALUES DATA3=$S2, I2,1H,,I1, F6.3*$
            VECTOR VALUES ANS1=$S13,I2,S7,I2,1H,I1,S5,F6.3,S4,F6.3,S4,
           1F8.5,S3,F8.5*$
            VECTOR VALUES ANS2=$1H0S5,54HFOR ALL LINES, THE EXTRAPOLATED
           1LATTICE PARAMETER IS  F8.5/S19, 41H THE SLOPE OF THE LEAST SQ
           1UARES LINE IS  F8.5/S7,  53H THE STANDARD DEVIATION OF THE LA
           1TTICE PARAMETER IS  F8.5*$
            VECTOR VALUES ANS3=$1H0S5,54HFOR THETA +30, THE EXTRAPOLATED
           1LATTICE PARAMETER IS  F8.5/S19, 41H THE SLOPE OF THE LEAST SQ
           1UARES LINE IS  F8.5/S7,  53H THE STANDARD DEVIATION OF THE LA
           1TTICE PARAMETER IS  F8.5*$
            END OF PROGRAM
$DATA
LAM1=1.78890, LAM2=1.79279*
42662NZ15DFC06.033.57515.572FE 21 16
 1 3,131.420
 2 8,130.040
 311,129.415
 412,129.220
 516,128.505
 624,127.260
 727,126.830
 832,126.140
 940,125.085
1043,124.695
1144,124.565
1248,124.045
1459,122.580
1564,121.875
1772,120.640
1872,220.585
1975,120.110
2075,220.050
2176,119.935
2280,119.110
2380,219.035
```

Computer Output

The following is the plotted output produced with the PLOT. subroutine along with a title and label for the abscissa produced using PRINT FORMAT statements. The output has been modified slightly (in an obvious fashion) to simplify its reproduction in this report.



Computer Output (continued)

The following is the printed output from the computer other than that associated with the plot.

FILM NO 42662 SPECIMEN NO NZ15DF
RADIATION CO EXPOSURE TIME 6.0 HRS
FILTER FE
CENTER 1 33.575 CENTER 2 15.572 SHRINK FACTOR= .49992

LINE NO	N1,J	RAD(L)	THETA	LATPA	NELRI
1	3,1	31.420	10.773	8.28813	5.14772
2	8,1	30.040	17.672	8.33383	2.96699
3	11,1	29.415	20.797	8.35531	2.43461
4	12,1	29.220	21.771	8.35383	2.29744
5	16,1	28.505	25.346	8.35778	1.87712
6	24,1	27.260	31.570	8.36980	1.35206
7	27,1	26.830	33.719	8.37234	1.21092
8	32,1	26.140	37.169	8.37482	1.01492
9	40,1	25.085	42.443	8.38253	.77104
10	43,1	24.695	44.393	8.38414	.69444
11	44,1	24.565	45.042	8.38447	.67031
12	48,1	24.045	47.642	8.38613	.58013
13	59,1	22.580	54.966	8.39072	.37300
14	64,1	21.875	58.490	8.39316	.29399
15	72,1	20.640	64.664	8.39736	.18243
16	72,2	20.585	64.939	8.39664	.17818
17	75,1	20.110	67.314	8.39574	.14392
18	75,2	20.050	67.614	8.39573	.13989
19	76,1	19.935	68.189	8.39589	.13235
20	80,1	19.110	72.313	8.39714	.08501
21	80,2	19.035	72.688	8.39805	.08128

FOR ALL LINES, THE EXTRAPOLATED LATTICE PARAMETER IS 8.39945
THE SLOPE OF THE LEAST SQUARES LINE IS -.02130
THE STANDARD DEVIATION OF THE LATTICE PARAMETER IS .00231

FOR THETA +3D, THE EXTRAPOLATED LATTICE PARAMETER IS 8.40001
THE SLOPE OF THE LEAST SQUARES LINE IS -.02309
THE STANDARD DEVIATION OF THE LATTICE PARAMETER IS .00099

Discussion of Results

A program of the type developed is mainly useful where a number of samples are to be examined of a known material. In effect, this spreads out the necessary set-up time, line identification and determination of plane indices over a number of specimens. As an example, this program has been used to follow solubility effects in materials containing an excess constituent as affected by annealing atmosphere, time, and temperature. Another application would be the study of minor phase precipitates in heat-resistant alloys subjected to elevated-temperature creep-exposure. Accurate cell measurements can also be used for such things as determining thermal expansion coefficients, phase boundaries in equilibrium diagrams, density measurement, and measurement of internal stresses (Reference 4).

The accuracy of the parameter determination depends (ultimately) on the resolution of the doublets in the back-reflection region of the Debye-Scherrer film. Various authorities

differ somewhat on the degree of accuracy attainable. The following tabulation indicates two opinions:

	Doublet Resolution	Accuracy Attainable - Per Cent Reference 3	Reference 4
1.	Well resolved, sharp	0.005 or better	0.001
2.	Resolved, but not sharp	0.02	0.2 - 0.02
3.	Not resolved		0.1
4.	High-angle lines too blurred to measure	1.0	1.0

In the example given, assuming a 2σ scatter-band (95% confidence) and using only angles greater than 30° in the extrapolation,

$a_o = 8.4000 \pm 0.0020\ A^{\circ}$ (rounding off to four places).

This corresponds to an accuracy of 0.024 per cent, a figure which appears to be reasonable for the resolved doublets in the film used in the example. (The material was a nickel-zinc ferrite.)

The plot function in this program has the main purpose of indicating which points have an excessive deviation from the least-squares extrapolation line. Since the experimental procedures are constant from film to film, it can be assumed that such a deviant point resulted from either an error in measurement or in indexing. It is then a simple matter to identify the suspect data, remove the card from the set of data cards, revise the identification card, and rerun the calculation. Alternatively, the program could be revised to perform a third extrapolation calculation, eliminating from consideration all points falling more than, say, 2σ from the line calculated in the second extrapolation.

The program reproduced above required 0.44 minutes for compilation and then executed five sets of data in 0.99 minutes. It is estimated that hand computation using a calculating machine and hand plotting of the results would require about three hours for each set of data.

Much more time would be saved when examining the more geometrically complex structures. For example, a comparable program could be written for the determination of the two parameters of hexagonal materials by the method of successive approximations, a process that might require as many as five trials before consistent results were obtained (Reference 4, page 482).

References

1. Klug, H. P. and L. E. Alexander, X-Ray Diffraction Procedures, John Wiley and Sons, Inc., New York, 1954.

2. Moroney, M. J., Facts from Figures, Penguin Books, Baltimore, Maryland, 1956.

3. Azaroff, L. V. and M. J. Buerger, The Powder Method in X-Ray Crystallography, McGraw-Hill Book Company, New York, 1958, p. 218.

4. Henry, N. F. M., Lipson, H. and W. A. Wooster., The Interpretation of X-Ray Diffraction Photographs, Macmillan and Company, London, 1960, pp. 191, 195.

5. Piazza, J. R., High Temperature Phase Equilibria in the System Carbon-Oxygen-Uranium, Ph.D. Thesis, The University of Michigan, 1961.

Example Problem No. 92

IONIC CRYSTAL STRUCTURE

by

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Department of Chemical and Metallurgical Engineering

The University of Michigan

Course: Physical Ceramics Credit hours: 4 Level: Senior

The following problem involves calculation of the Madelung Constant for an AX compound. It may be assigned in one of two ways:

1. The student may be required to decide on a suitable computational technique, program the solution, and check the program using appropriate test data.
2. The student may be required only to analyze the crystal structure for one or more ionic crystals and prepare the data in a form suitable for submission to a program pre-written by the instructor.

This description of the problem and its solution are presented in detail sufficient for the first method of assignment (i.e., the student writes the program). In practice, however, the problem has only been assigned in the second manner (i.e., the student just prepares the data) The advantages of the second method of assignment are discussed in the critique.

Statement of Problem

The Madelung Constant, A_m, is a ratio between the potential energy, E_c, of an ion within a crystal lattice as compared with the energy, E_{pr}, between a single pair of ions; thus

$$A_m = E_c/E_{pr}$$

The calculation of the Madelung Constant is achieved through the summation of coulombic attractions and repulsions. In strict mathematical terms the calculation may be achieved as

$$A_m = \frac{1}{2}\sum_{i,j}\left(\frac{q_i}{q_+}\right)\cdot\left(\frac{q_j}{q_-}\right)\cdot\left(\frac{d}{r_{i,j}}\right)$$

However, any methodical procedure for selecting the three-dimensional lattice gives a series which converges extremely slowly, if at all , unless appropriate mathematical manipulations are made.

(1) Select a procedure and write a program for the solution of the Madelung Constant.

(2) Provide appropriate data from the crystal structure to solve the Madelung Constant, checking the result against known answers.

(3) Discuss any limitations in the program imposed by the method selected for the program.

Solution

The mathematical manipulation followed in the technique which is outlined below involves establishing a sphere surrounding a reference ion and calculating the attraction and repulsion forces between the reference ion and each ion within the selected radius; more remote ions are discarded. This method of calculation is valid for any AX compound regardless of crystal structure. It may also be used to determine the Madelung constant for ions on or in the surface, edge, or corner of the crystals with ((100)) faces.

As presently programmed, the calculation can not be made for non-AX compounds or for other crystal surfaces*. The program could be modified to do so; however, it is not recommended that such an assignment be given to the ordinary student because of time limitations. The present program is sufficient to emphasize the order and pattern of NaCl-, ZnS-, ZnO-, CsCl-, and FeS-type structures. If desired, it may also be used to show the origin of surface energies.

The student must supply data as follows which pertain to the crystal structure:

1. The crystal system and type.
2. The number of ions per unit cell.
3. The lattice constant and the reference dimension which is the closest approach of ions.
4. The ion charges, and their location within the unit cell.

In addition he must put limits on his calculation as follows:

5. The sphere size for calculation (in angstroms).
6. The crystal block (in unit cell dimensions) which is large enough to enclose the sphere, but which avoids excessive calculations outside the sphere.

Additional information may be supplied, stating the amount of intermediate printing which is desired as follows:

7. Whether intermediate parameters calculated for each cell, for only the cell with X = 0, Y = 0, and Z = 0, or no intermediate parameters are to be printed.

The above required data are illustrated in the table below where MgO is used as an example. The data are given in a form which may be read by the computer program using the simplified-input (READ DATA) statement in the MAD language. The definitions of the symbols are given in the next section.

---

* However, other crystal surfaces may be obtained by selecting non-conventional unit cells of these AX crystal types, e.g., the primitive cell of NaCl will give the ((111)) faces of the regular cell.

EXAMPLE DATA SUPPLIED TO THE PROGRAM FOR MgO

Crystal Properties

STRUCT = $CUBIC$, TYPE = MGO, NION = 8

A = 4.203

REFDIM = 2.1015

CHARGE(0) = -2, U(0) = 0.0, V(0) = 0.0, W(0) = 0.0,

CHARGE(1) = +2, U(1) = 0.5, V(1) = 0.0, W(1) = 0.0,

CHARGE(2) = -2, U(2) = 0.5, V(2) = 0.0, W(2) = 0.5,

CHARGE(3) = +2, U(3) = 0.0, V(3) = 0.5, W(3) = 0.0,

CHARGE(4) = -2, U(4) = 0.5, V(4) = 0.5, W(4) = 0.0,

CHARGE(5) = +2, U(5) = 0.0, V(5) = 0.0, W(5) = 0.5,

CHARGE(6) = -2, U(6) = 0.0, V(6) = 0.5, W(6) = 0.5,

CHARGE(7) = +2, U(7) = 0.5, V(7) = 0.5, W(7) = 0.5,

Limits

RLIMIT = 8.405

UPPERX = +2, UPPERY = +2, UPPERZ = +2,

LOWERX = -2, LOWERY = -2, LOWERZ = -2,

Print-out Options for Intermediate Calculations

TRIAL = $CENTER$*

List of Symbols

The following are the important symbols used in the MAD program with their definitions.

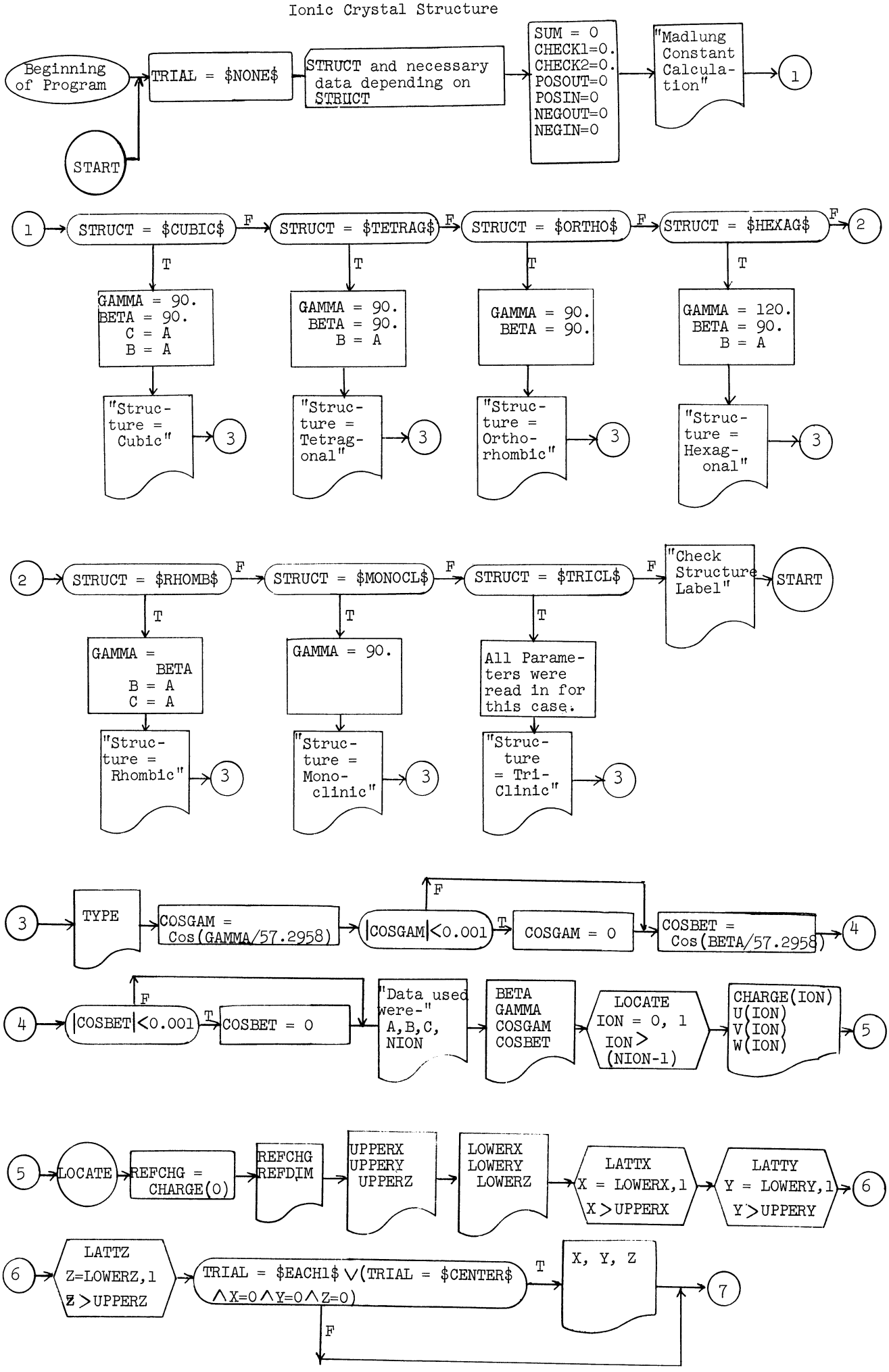
ADDON	CHARGE(ION)/R3DIM, angstroms
A	unit cell dimension, angstroms
BETA	axial angle between Y and Z axes, degrees
B	unit cell dimension, angstroms
CELLCK	sum from cell for X = 0, Y = 0, Z = 0, normalized to REFDIM = 1, also equals (CHECK2-CHECK1)/REFDIM
CHARGE(ION)	array containing charge carried by each ion (ION)
CHECK1	sum prior to beginning calculation for any cell
CHECK2	sum after completing calculation for any cell
COSBET	cosine of BETA
COSGAM	cosine of GAMMA
C	unit cell dimension, angstroms
GAMMA	axial angle between X and Y axes, degrees
ION	counter for each ion within the unit cell

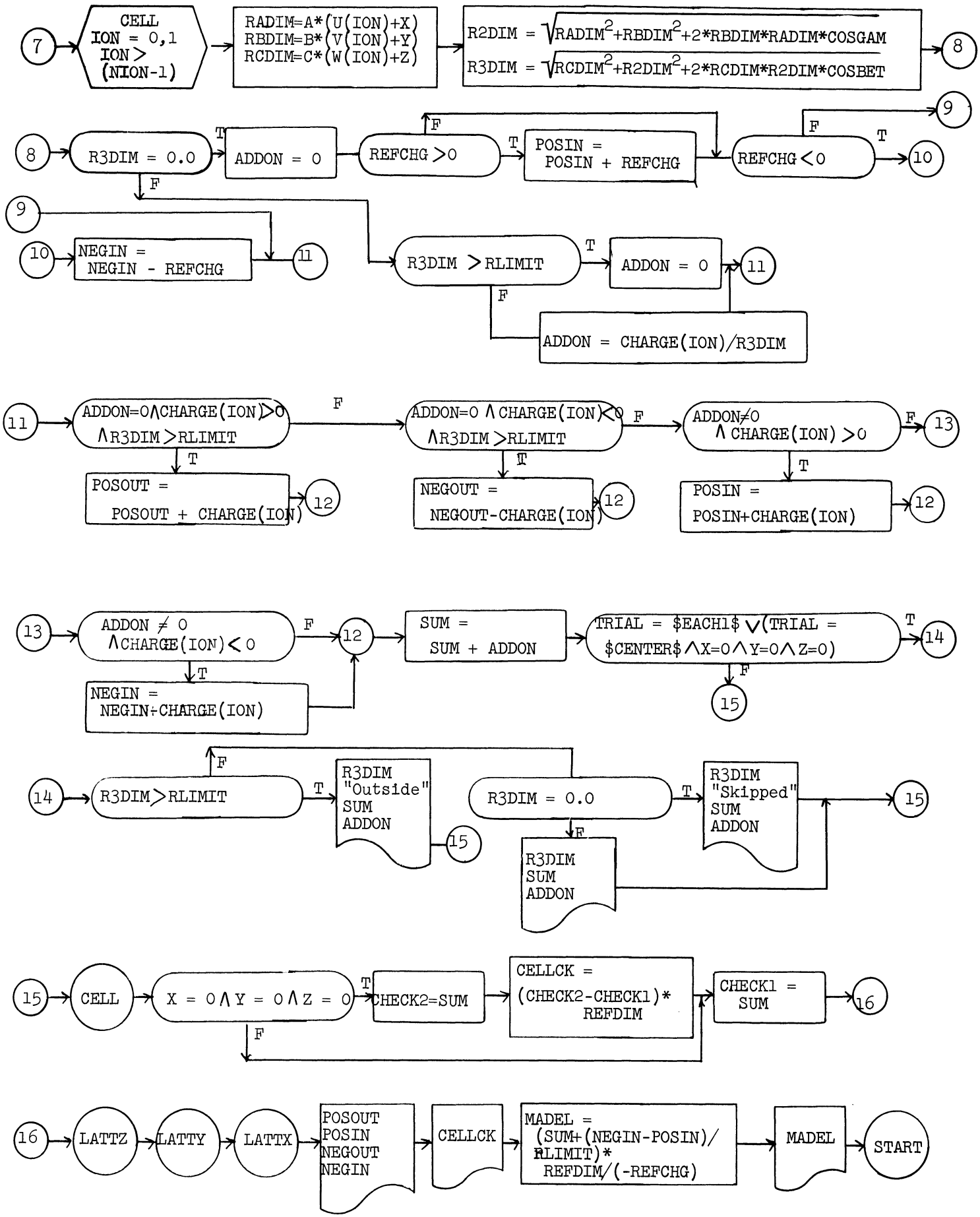
LOWERX LOWERY LOWERZ	lower limit of cell scans in X-direction, Y-direction, and Z-direction, respectively
MADEL	Madelung Constant
NEGIN	negative charges within sphere*
NEGOUT	negative charges discarded (outside sphere)
NION	number of ions per unit cell
POSIN	positive charges within sphere*
POSOUT	positive charges discarded (outside sphere)
R2DIM	X-Y plane distance between reference ion and particular ion being considered, angstroms
R3DIM	three-dimensional distance between reference ion and particular ion being considered, angstroms
RADIM	A*(U(ION)+X)
RBDIM	B*(V(ION)+Y)
RCDIM	C*(W(ION)+Z)
REFCHG	charge of reference ion, in electron units
REFDIM	closest approach of two ions, angstroms
RLIMIT	radius of calculation sphere (It is best if this radius equals the distance to the closest surface ion.)
SUM	variable for storing cumulative results of integration of ADDON
STRUCT	variable containing alphabetic code for crystal structure: STRUCT = $CUBIC$, $TETRAG$, $ORTHO$, $HEXAG$, $RHOMB$, $MONOCL$, or $TRICL$, depending on whether structure is cubic, tetragonal, orthorhombic, hexagonal, rhombic, monoclinic, or triclinic, respectively.
TRIAL	variable containing alphabetic code to control intermediate printing: TYPE = $EACH1$, $CENTER$, or $NONE$ depending on whether intermediate printing is desired for each cell, only for the center cell, or not at all, respectively.
TYPE	variable containing alphabetic code for type of crystal, examples are $CSCL$ for CsCl, $NACL$, for NaCl, and FES for FeS
UPPERX UPPERY UPPERZ	upper limit of cell scans in X-direction, Y-direction, and Z-direction, respectively
U(ION) V(ION) W(ION)	fractional cell location in X-direction, Y-direction, and Z-direction, respectively of each ion (ION),
X Y Z	indices in matrix of cells in X-direction, Y-direction, and Z-direction, respectively

---

* if POSIN $\neq$ NEGIN, the program places the balancing number of ions on the surface of the sphere. This necessary approximation may place some variation in the second decimal place of the Madelung constant if there is a big difference between POSIN and NEGIN.

Ionic Crystal Structure




7
CELL
ION = 0,1
ION > (NION-1)
RADIM=A*(U(ION)+X)
RBDIM=B*(V(ION)+Y)
RCDIM=C*(W(ION)+Z)
R2DIM = √(RADIM²+RBDIM²+2*RBDIM*RADIM*COSGAM
R3DIM = √(RCDIM²+R2DIM²+2*RCDIM*R2DIM*COSBET
8
8
R3DIM = 0.0
T
ADDON = 0
F
REFCHG >0
T
POSIN = POSIN + REFCHG
F
REFCHG <0
T
10
9
9
10
NEGIN = NEGIN - REFCHG
11
R3DIM > RLIMIT
T
ADDON = 0
11
F
ADDON = CHARGE(ION)/R3DIM
11
ADDON=0∧CHARGE(ION)>0 ∧R3DIM>RLIMIT
F
ADDON=0 ∧CHARGE(ION)<0 ∧R3DIM>RLIMIT
F
ADDON≠0 ∧CHARGE(ION) >0
F
13
T
POSOUT = POSOUT + CHARGE(ION)
12
T
NEGOUT = NEGOUT-CHARGE(ION)
12
T
POSIN = POSIN+CHARGE(ION)
12
13
ADDON ≠ 0 ∧CHARGE(ION)<0
F
12
T
NEGIN = NEGIN+CHARGE(ION)
SUM = SUM + ADDON
TRIAL = $EACH1$ ∨(TRIAL = $CENTER$∧X=0∧Y=0∧Z=0)
T
14
F
15
14
F
R3DIM>RLIMIT
T
R3DIM "Outside" SUM ADDON
15
R3DIM = 0.0
T
R3DIM "Skipped" SUM ADDON
15
F
R3DIM SUM ADDON
15
CELL
X = 0∧Y = 0∧Z = 0
T
CHECK2=SUM
CELLCK = (CHECK2-CHECK1)* REFDIM
CHECK1 = SUM
16
F
16
LATTZ
LATTY
LATTX
POSOUT POSIN NEGOUT NEGIN
CELLCK
MADEL = (SUM+(NEGIN-POSIN)/RLIMIT)* REFDIM/(-REFCHG)
MADEL
START

MAD Program

```
    L. H. VAN VLACK              S225B              002   050   000      MADLUNG
    L. H. VAN VLACK              S225B              002   050   000      MADLUNG
    L. H. VAN VLACK              S225B              002   050   000      MADLUNG
 $COMPILE MAD,EXECUTE,DUMP,PRINT OBJECT, PUNCH OBJECT
          INTEGER X,Y,Z,ION,NION,UPPERX,UPPERY,UPPERZ,LOWERX,LOWERY,
         1    LOWERZ,STRUCT,TYPE,HOLD,TRIAL,POSOUT,POSIN,NEGOUT,NEGIN
          DIMENSION CHARGE(100),U(100),V(100),W(100)
 START    TRIAL = $NONE$
          READ DATA
          SUM=0
          CHECK1=0.
          CHECK2=0.
          POSOUT = 0
          POSIN = 0
          NEGOUT = 0
          NEGIN = 0
          PRINT COMMENT $1                          **********
         1**********$
          PRINT COMMENT $                           * MADELUNG CONSTAN
         1T CALCULATION *                                    SPHERE$
          PRINT COMMENT $                           **********
         1**********$
          WHENEVER STRUCT.E.$CUBIC$
          GAMMA=90.
          BETA=90.
          B=A
          C=A
          PRINT COMMENT$0     STRUCTURE = CUBIC$
          OR WHENEVER STRUCT.E.$TETRAG$
          GAMMA=90.
          BETA=90.
          B=A
          PRINT COMMENT$0     STRUCTURE = TETRAGONAL$
          OR WHENEVER STRUCT.E.$ORTHO$
          GAMMA=90.
          BETA=90.
          PRINT COMMENT$0     STRUCTURE = ORTHORHOMBIC$
          OR WHENEVER STRUCT.E.$HEXAG$
          GAMMA=120.
          BETA=90.
          B=A
          PRINT COMMENT$0     STRUCTURE = HEXAGONAL$
          OR WHENEVER STRUCT.E.$RHOMB$
          GAMMA=BETA
          B=A
          C=A
          PRINT COMMENT$0     STRUCTURE = RHOMBIC$
          OR WHENEVER STRUCT.E.$MONOCL$
          GAMMA=90.
          PRINT COMMENT$0     STRUCTURE = MONOCLINIC$
          OR WHENEVER STRUCT.E.$TRICL$
          PRINT COMMENT$0     STRUCTURE = TRICLINIC$
          OTHERWISE
          PRINT COMMENT$0CHECK STRUCTURE LABEL$
          TRANSFER TO START
          END OF CONDITIONAL
          PRINT FORMAT XTAL, TYPE
          VECTOR VALUES XTAL = $1H0,S10, 7HTYPE =    C6*$
          PRINT COMMENT$      ---------   ---          $
          COSGAM = COS.(GAMMA/57.2958)
          WHENEVER .ABS. COSGAM .L. 0.001, COSGAM = 0.0
          COSBET = COS.(BETA /57.2958)
          WHENEVER .ABS. COSBET .L. 0.001, COSBET = 0.0
          PRINT COMMENT$0DATA USED WERE-$
          PRINT RESULTS A,B,C,NION
          PRINT RESULTS BETA, GAMMA,COSGAM, COSBET
          THROUGH LOCATE, FOR ION=0,1,ION.G.(NION-1)
 LOCATE   PRINT RESULTS CHARGE(ION),U(ION),V(ION),W(ION)
          REFCHG=CHARGE(0)
          PRINT COMMENT$-REFERENCE CHARGE IS CHARGE OF ION AT U(0), V(0
         1), W(0)$
          PRINT RESULTS REFCHG
```

MAD Program (continued)

```
          PRINT COMMENT$-REFERENCE DIMENSION IS THE CLOSEST APPROACH OF
         1 POSITIVE AND NEGATIVE IONS$
          PRINT FORMAT RFORM, $REFDIM$, REFDIM
          VECTOR VALUES RFORM = $1HO,S8,C6,3H = ,F12.6,10H ANGSTROMS *$
          PRINT COMMENT $-LIMITS USED WERE-$
          PRINT RESULTS UPPERX,UPPERY,UPPERZ
          PRINT RESULTS LOWERX,LOWERY,LOWERZ
          PRINT COMMENT $                                THE UPPER AND LOWER
         1LIMITS ARE IN UNIT CELL DIMENSIONS$
          PRINT FORMAT RFORM, $RLIMIT$, RLIMIT
          PRINT COMMENT $-                    $
          THROUGH LATTX, FOR X=LOWERX,1,X.G.UPPERX
          THROUGH LATTY, FOR Y=LOWERY,1,Y.G.UPPERY
          THROUGH LATTZ, FOR Z=LOWERZ,1,Z.G.UPPERZ
          WHENEVER TRIAL.E.$EACH1$.OR.(          TRIAL.E.$CENTER$.AND.
         1X.E.0.AND.Y.E.0.AND.Z.E.0)
              PRINT RESULTS X, Y, Z
              PRINT COMMENT $ $
          END OF CONDITIONAL
          THROUGH CELL, FOR ION=0,1,ION.G.(NION-1)
          RADIM=A*(U(ION)+X)
          RBDIM=B*(V(ION)+Y)
          RCDIM=C*(W(ION)+Z)
          R2DIM=SQRT.(RADIM.P.2+RBDIM.P.2+2*RADIM*RBDIM*COSGAM)
          R3DIM=SQRT.(RCDIM.P.2+R2DIM.P.2+2*RCDIM*R2DIM*COSBET)
          WHENEVER R3DIM.E.0.0
          ADDON = 0.0
          WHENEVER REFCHG.G.0,POSIN=POSIN+REFCHG
          WHENEVER REFCHG.L.0,NEGIN=NEGIN-REFCHG
          OR WHENEVER .ABS. R3DIM .G. RLIMIT
          ADDON = 0.0
          OTHERWISE
          ADDON = CHARGE(ION)/R3DIM
          END OF CONDITIONAL
          WHENEVER ADDON.E.0.AND.CHARGE(ION).G.0.AND.R3DIM.G.RLIMIT
          POSOUT=POSOUT+CHARGE(ION)
          OR WHENEVER ADDON.E.0.AND.CHARGE(ION).L.0.AND.R3DIM.G.RLIMIT
          NEGOUT=NEGOUT-CHARGE(ION)
          OR WHENEVER ADDON.NE.0.AND.CHARGE(ION).G.0
          POSIN=POSIN+CHARGE(ION)
          OR WHENEVER ADDON.NE.0.AND.CHARGE(ION).L.0
          NEGIN=NEGIN-CHARGE(ION)
          END OF CONDITIONAL
          SUM = SUM + ADDON
          WHENEVER TRIAL.E.$EACH1$.OR.(          TRIAL.E.$CENTER$.AND.
         1X.E.0.AND.Y.E.0.AND.Z.E.0)
          WHENEVER R3DIM.G.RLIMIT
          PRINT COMMENT $+                                   OUTSIDE$
          OR WHENEVER R3DIM.E.0.0
          PRINT COMMENT $+                                   SKIPPED$
          END OF CONDITIONAL
          PRINT FORMAT ANSALL, R3DIM, SUM, ADDON
          VECTOR VALUES ANSALL = $S6, 8HR3DIM =    F12.6,S22,6HSUM =
         1F12.6,S16,12HINCREMENT =    F12.6*$
          END OF CONDITIONAL
CELL      CONTINUE
          WHENEVER X.E.0.AND.Y.E.0.AND.Z.E.0
          CHECK2=SUM
          CELLCK = (CHECK2-CHECK1)*REFDIM
          END OF CONDITIONAL
          CHECK1=SUM
LATTZ     CONTINUE
LATTY     CONTINUE
LATTX     CONTINUE
          PRINT RESULTS POSOUT, POSIN, NEGOUT, NEGIN
          PRINT FORMAT CFORM, $CELLCK$, CELLCK
          VECTOR VALUES CFORM = $1HO, S8, C6, 3H = , F12.6, S9,
         1   78HCELLCK IS THE SUM FROM CELL FOR X = 0, Y = 0, Z = 0 NOR
         2MALIZED TO REFDIM = 1        *$
          MADEL=(SUM+(NEGIN-POSIN)/RLIMIT)*REFDIM/(-REFCHG)
          PRINT COMMENT $0                          **********************
         1*************$
          PRINT FORMAT ANSWER , MADEL
          VECTOR VALUES ANSWER = $47H+                                MADELUN
         1G CONSTANT = , F9.3*$
          PRINT COMMENT $                           *
         1             *$
          PRINT COMMENT $                           **********************
         1*************$
          TRANSFER TO START
          END OF PROGRAM
```

Data

```
$DATA
 STRUCT=$CUBIC$,TYPE=$MGO $,NION=8
 TRIAL=$NONE$
 A=4.203
 REFDIM=2.1015
 UPPERX=+2,LOWERX=-2,UPPERY=+2,LOWERY=-2
 UPPERZ=+2,LOWERZ=-2
 RLIMIT = 8.405
 CHARGE(0)=-2, U(0)=0.0, V(0)=0.0, W(0)=0.0
 CHARGE(1)=+2, U(1)=0.5, V(1)=0.0, W(1)=0.0
 CHARGE (2)=-2, U(2)=0.5, V(2)=0.0, W(2)=0.5
 CHARGE (3)=+2, U(3)=0.0, V(3)=0.5, W(3)=0.0
 CHARGE (4)=-2, U(4)=0.5, V(4)=0.5, W(4)=0.0
 CHARGE (5)=+2, U(5)=0.0, V(5)=0.0, W(5)=0.5
CHARGE (6)=-2, U(6)=0.0, V(6)=0.5, W(6)=0.5
 CHARGE (7)=+2, U(7)=0.5, V(7)=0.5, W(7)=0.5          *
 STRUCT=$CUBIC$,TYPE=$BLENDE$, NION=8
 A=5.412
 RLIMIT = 10.82
 REFDIM = 2.35
 UPPERX=+2,LOWERX=-2,UPPERY=+2,LOWERY=-2
 UPPERZ=+2,LOWERZ=-2
 CHARGE(0)=-2, U(0)=0.0, V(0)=0.0, W(0)=0.0
 CHARGE(1)=+2, U(1)=0.75,V(1)=0.75,W(1)=0.75
 CHARGE (2)=-2, U(2)=0.5, V(2)=0.0, W(2)=0.5
 CHARGE (3)=+2, U(3)=0.25, V(3)=0.25, W(3)=0.75
 CHARGE (4)=-2, U(4)=0.5, V(4)=0.5, W(4)=0.0
 CHARGE (5)=+2, U(5)=0.75,V(5)=0.25,W(5)=0.25
 CHARGE (6)=-2, U(6)=0.0, V(6)=0.5, W(6)=0.5
 CHARGE (7)=+2, U(7)=0.25,V(7)=0.75,W(7)=0.25
 STRUCT=$HEXAG$, TYPE=$WURTZI$, NION=4
 A=3.811    , C=6.234
 RLIMIT = 11.25
 REFDIM = 2.34
 UPPERX=+3,LOWERX=-3,UPPERY=+3,LOWERY=-3
 UPPERZ=+2,LOWERZ=-3
 CHARGE(0)=-2, U(0)=0.0, V(0)=0.0, W(0)=0.0
 CHARGE(1)=+2, U(1)=0.0  ,V(1)=0.0,W(1)=0.375
 CHARGE (2)=-2, U(2)=0.333333,V(2)=0.666667,W(2)=0.5
 CHARGE (3)=+2, U(3)=0.333333,V(3)=0.666667,W(3)=0.875    *
 STRUCT=$HEXAG$, TYPE=$FES$, NION=4
 A = 3.535
 C = 5.774
 RLIMIT = 12.00
 REFDIM=2.5
 UPPERX=+3,LOWERX=-4, UPPERY=+3, LOWERY=-4
 UPPERZ=+2,LOWERZ=-3
 CHARGE(0)=+2, U(0)=0.    ,V(0)=0.    ,W(0)=0.
 CHARGE(1)=-2, U(1)=0.666667 ,V(1)=0.333333 ,W(1)=0.25
 CHARGE(2)=+2, U(2)=0.333333 ,V(2)=0.666667 ,W(2)=0.50
 CHARGE(3)=-2, U(3)=0.666667 ,V(3)=0.333333 ,W(3)=0.75     *
 STRUCT=$CUBIC$,TYPE=$CSCL$,NION=2
 A=4.110
 REFDIM =3.559
 RLIMIT = 8.21
UPPERX=+2,LOWERX=-2,UPPERY=+2,LOWERY=-2
 UPPERZ=+2,LOWERZ=-2
 CHARGE(0)=-1, U(0)=0.0, V(0)=0.0, W(0)=0.0
 CHARGE(1)=+1, U(1)=0.5, V(1)=0.5, W(1)=0.5          *
```

Computer Output

A typical set of computer output is shown on the next page. This corresponds to the first set of data shown with the MAD program above. An example was selected with no intermediate printing to conserve space in this report.

Computer Output

```
                    **********************************
                    * MADELUNG CONSTANT CALCULATION *                    SPHERE
                    **********************************

STRUCTURE = CUBIC

     TYPE = MGO

DATA USED WERE-

        A =  4.2030,       B =  4.2030,       C =  4.2030,     NION = 8
     BETA = 90.0000,   GAMMA = 90.0000,  COSGAM =   .0000,  COSBET =  .0000
CHARGE(0) = -2.0000,    U(0) =   .0000,    V(0) =   .0000,    W(0) =  .0000
CHARGE(1) =  2.0000,    U(1) =   .5000,    V(1) =   .0000,    W(1) =  .0000
CHARGE(2) = -2.0000,    U(2) =   .5000,    V(2) =   .0000,    W(2) =  .5000
CHARGE(3) =  2.0000,    U(3) =   .0000,    V(3) =   .5000,    W(3) =  .0000
CHARGE(4) = -2.0000,    U(4) =   .5000,    V(4) =   .5000,    W(4) =  .0000
CHARGE(5) =  2.0000,    U(5) =   .0000,    V(5) =   .0000,    W(5) =  .5000
CHARGE(6) = -2.0000,    U(6) =   .0000,    V(6) =   .5000,    W(6) =  .5000
CHARGE(7) =  2.0000,    U(7) =   .5000,    V(7) =   .5000,    W(7) =  .5000

REFERENCE CHARGE IS THE CHARGE OF ION AT U(0), V(0), W(0)
     REFCHG = -2.000

REFERENCE DIMENSION IS THE CLOSEST APPROACH OF POSITIVE AND NEGATIVE IONS
     REFDIM =  2.1015  ANGSTROMS

LIMITS USED WERE--

  UPPERX =  2,   UPPERY =  2,   UPPERZ =  2
  LOWERX = -2,   LOWERY = -2,   LOWERZ = -2
       THE UPPER AND LOWER LIMITS ARE IN UNIT CELL DIMENSIONS

  RLIMIT =  8.4050  ANGSTROMS


  POSOUT =  768,   POSIN =  232,   NEGOUT =  730
  CELLCK = 2.912,   NEGIN =  270

CELLCK IS THE SUM FROM CELL FOR X = 0, Y = 0, Z = 0 NORMALIZED TO REFDIM = 1

                    **********************************
                    * MADELUNG CONSTANT  =  1.742    *
                    **********************************
```

Discussion of Results

Results have been obtained for several different crystal structures. The numerical values of the Madelung Constants which were calculated by the program are listed below along with the generally accepted value where available.

Crystal Structure	Madelung Constant Calculated by Program	Generally Accepted Value*
NaCl	1.744	1.747
CaCl	1.776	1.762
ZnS (Blends)	1.633	1.638
ZnS (Wurtzite)	1.567	1.641
FeS	1.745	---
MgO	1.742	1.747

It can be seen that the computational technique utilized by the program give values of the Madelung Constant which is generally accurate to about two decimal places.

Critique

Experience in several classes has indicated that the calculation of the Madelung Constant serves as a very useful teaching procedure. Successful results have been obtained by requiring the student only to prepare appropriate data for submission to a program pre-written by the instructor. This avoids having the students spend an undue amount of time on the problem.

In order to supply the correct data the student must understand the crystal structure of his problem more thoroughly than he would from simply reading descriptions in a textbook. The problem solution then serves to check him and, in fact, provides him with a means of analyzing his structure for errors if he receives an incorrect answer.

---

* Sherman, Chemical Review, 11, 93 (1932)

Example Problem No. 93

UNSTEADY-STATE HEAT CONDUCTION IN SOLIDIFYING ALLOY

by

J. R. Street and J. O. Wilkes

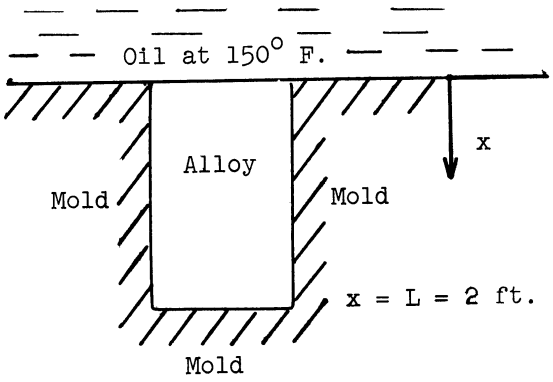
Department of Chemical and Metallurgical Engineering

The University of Michigan

Course: Rate Operations Credit hours: 5 Level: Junior

Statement of Problem

A cylindrical mold is to be charged with a molten alloy at an initial temperature of 400°F., the liquidus temperature of the alloy. The mold is well insulated except at one end, which is maintained at the solidus temperature of the alloy, 150°F., by a stream of oil. The geometry is indicated in the figure at the right.



By (a) setting up the partial differential equation and appropriate boundary and initial conditions to describe the temperature $\Theta(x,t)$ of the solidifying ingot as a function of distance x and time t, and (b) reducing the partial differential equations and associated conditions to appropriate finite difference forms, calculate the temperature profiles in the ingot as a function of time. Also, determine the time required for the face x = 2 ft. to cool to 200°F.

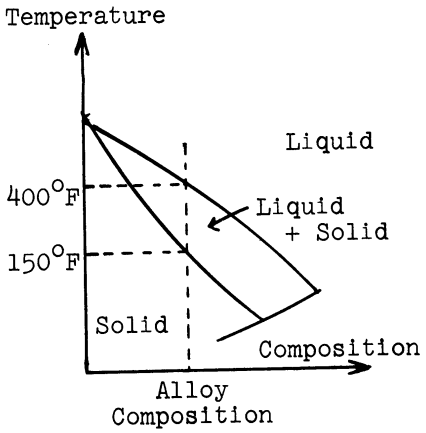
The following data are available for the alloy:

$\rho_{liquid} = \rho_{solid} = 540$ lb./cu.ft.

$k_{liquid} = k_{solid} = 10.1$ B.Th.U./hr.ft.°F.

$(c_p)_{liquid} = (c_p)_{solid} = 0.038$ B.Th.U./lb.°F.

ΔH = heat of fusion of the alloy = 120.0 B.Th.U./lb.



The quantity $\alpha(\Theta)$, given in the table on the following page as a function of temperature Θ, has been determined from the phase equilibrium diagram shown in the figure at the right. It gives the amount of solid formed corresponding to a small drop in temperature of the liquid/solid mixture.

Unsteady-State Heat Conduction in Solidifying Alloy

Values of $\alpha(\theta)$ = lbs. solid formed per °F.

per lb. mixture of solid and liquid.

θ (°F)	$-\alpha(\theta)$	θ (°F)	$-\alpha(\theta)$	θ (°F)	$-\alpha(\theta)$	θ (°F)	$-\alpha(\theta)$
150	0.0119	220	0.00454	290	0.00252	360	0.00173
160	0.0102	230	0.00412	300	0.00238	370	0.00167
170	0.00874	240	0.00375	310	0.00223	380	0.00160
180	0.00756	250	0.00341	320	0.00211	390	0.00153
190	0.00657	260	0.00315	330	0.00200	400	0.00147
200	0.00575	270	0.00291	340	0.00190		
210	0.00509	280	0.00270	350	0.00181		

Solution

By performing a heat balance on a differential element, and taking into account a generation term arising from latent heat effects, the differential equation giving the alloy temperature $\theta(x,t)$ as a function of distance x and time t is found to be

$$\frac{\partial^2\theta}{\partial x^2} = \frac{\rho}{k}(c_p - \alpha\Delta H)\frac{\partial\theta}{\partial t} \qquad (1)$$

where $\alpha = \alpha(\theta)$ is a known function of temperature, there being no heat conduction in the y direction. Equation (1) is subject to the boundary and initial conditions,

$$\theta(0,t) = 150\ °F \quad \text{for} \quad t \geqslant 0 \qquad (1a)$$

$$\frac{\partial\theta}{\partial x}(L,t) = 0 \quad \text{for } t \not\geqslant 0, \text{ at } L = 2.0 \text{ ft.} \qquad (1b)$$

$$\theta(x,0) = 400\ °F \quad \text{for} \quad 0 \leqslant x \leqslant L \qquad (1c)$$

In the finite difference method of solution, the interval $0 \leqslant x \leqslant L$ is divided into a grid of points spaced Δx apart, and temperatures at all grid points are computed at time intervals of Δt. Replacement of $\partial^2\theta/\partial x^2$ and $\partial\theta/\partial t$ by their finite difference approximations yields the following finite difference representation of equation (1);

$$\theta(x+\Delta x,t+\Delta t) - 2\theta(x,t+\Delta t) + \theta(x-\Delta x,t+\Delta t) = \frac{\rho}{k}(c_p - \alpha\Delta H)\frac{(\Delta x)^2}{\Delta t}\left[\theta(x,t+\Delta t)-\theta(x,t)\right] \qquad (2)$$

The choice of approximation of $\partial^2\theta/\partial x^2$ from temperatures not at time t, but at time $t+\Delta t$, has led to an "implicit" finite difference form. In general, the $\theta(x,t)$ will be known and the $\theta(x,t+\Delta t)$ will have to be calculated from equation (2) applied at each grid point. This requires the solution of a set of N simultaneous equations (where N = number of grid points), but does not suffer from the restriction on the size of Δt which attends the alternative "explicit" form.

Let I designate the grid point with x coordinate = $I\Delta x$; I may have any value from 0,1,2...to N Then, in order to simplify programming, the number of subscripts on θ may be reduced from two to one by introducing the variables:

S(I) = value of θ at grid point I and time level t

T(I) = value of θ at grid point I and time level $t+\Delta t$

With this new notation, and substituting

$$\Gamma(I) = \frac{\rho}{k}(c_p - \alpha \Delta H)\frac{(\Delta x)^2}{\Delta t} \qquad (3)$$

Equation (2) becomes

$$T(I) = \frac{T(I+1) + T(I-1) + \Gamma(I)\cdot S(I)}{\Gamma(I) + 2} \qquad (4)$$

In equation (4), the "old" temperature S(I) will be known at all grid points I = 0,1,...,N. From a table look-up procedure the corresponding values of α and hence the values of $\Gamma(I)$ can be found. Successively better approximations for the "new" temperatures T(I) are obtained by repeated application of equation (4). As a starting guess it is convenient to put T(I)=S(I). The iteration is repeated until the T(I) have converged sufficiently; a suitable criterion for stopping is when the sum ε of the absolute values of the deviations of the T(I) from their last computed value is less than some arbitrarily small quantity ε_{max}. At this stage the T(I) are then called "old" temperatures and are substituted into the S(I) and the process is carried on for as many time-steps as is desired. In the present case, computation was stopped when T(N) had dropped to 200 °F.

Boundary condition (1a) dictates that S(0) = T(0) = 150 for all values of t. The initial condition (1c) sets S(I) = 400 for I=1,2,...,N at t = 0. Boundary condition (1b) requires that, instead of using equation (4), the temperature T(N) at the last grid point N should be computed fromequation (5):

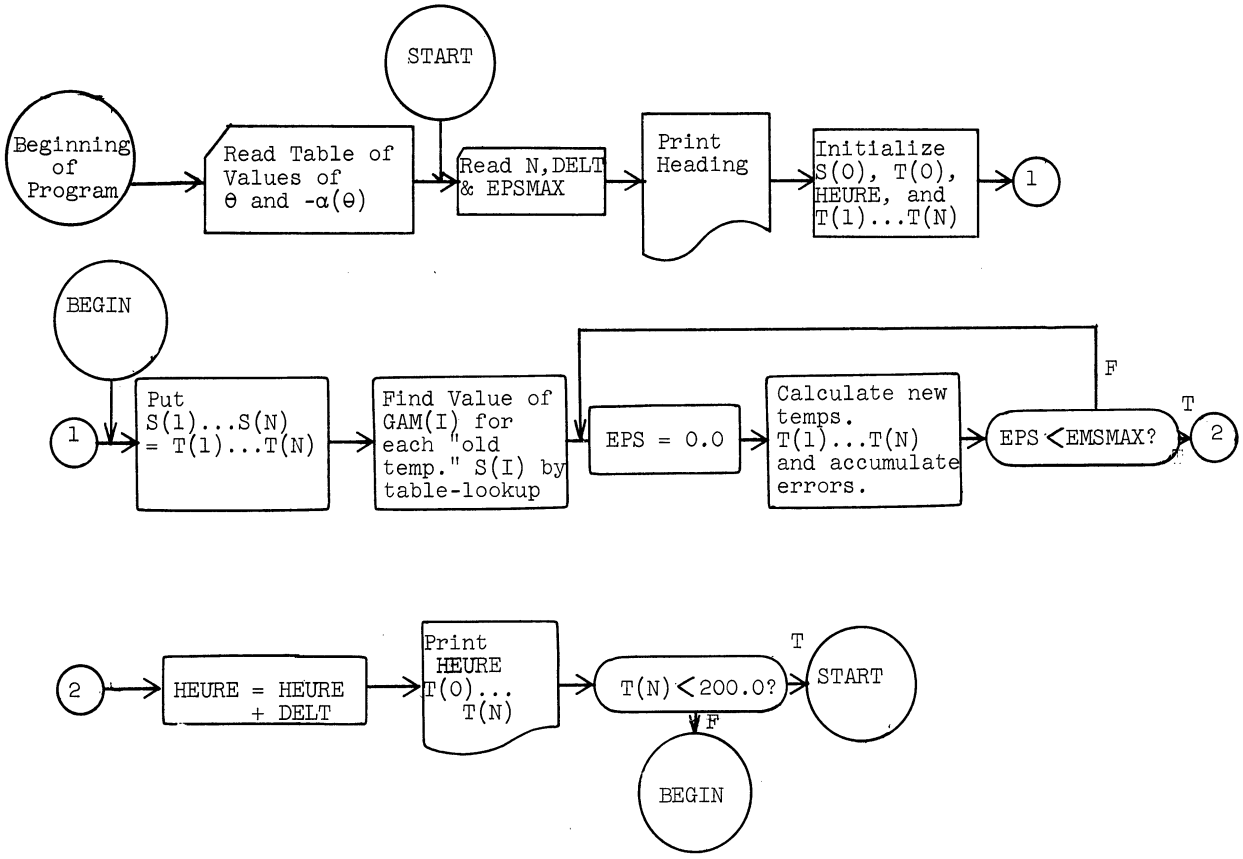
$$T(N) = \frac{2T(N-1) + \Gamma(N)S(N)}{\Gamma(N) + 2} \qquad (5)$$

List of Symbols

MAD Symbol	Definition
T(I)	"New" temperature at point I
S(I)	"Old" temperature at point I
J	iteration parameter for table look-up
Y(J)	table look-up values of temperature
X(J)	table look-up values of $-\alpha$
A	$-\alpha$
GAM(I)	value of $\Gamma(I) = \frac{\rho}{k}(c - \alpha\Delta H)$ corresponding to S(I)
B	$\frac{\rho}{k}\frac{(\Delta x)^2}{\Delta t}$
DELT	Δt (time increment)
HEURE	total time from start
EPS	sum of absolute values of deviations of the T(I) from their last computed values

EPSMAX	ε_{max} = largest tolerable value of EPS
K	counter on the number of iterations required to compute T to required accuracy at any one time level.
N	index of last grid point (number of grid points = N+1)
I	index for grid points ($0 \leq I \leq N$)

Flow Diagram



MAD Program and Data

```
 J. O. WILKES                    X137N          005   040   000      JOW08
 J. O. WILKES                    X137N          005   040   000      JOW08
$ COMPILE MAD, EXECUTE
          R    SOLIDIFICATION OF AN INGOT
           INTEGER I, J, K, N                                        JOW08010
           DIMENSION S(30), T(30), GAM(30), X(30), Y(30)             JOW08020
           READ FORMAT TABLE, X(0)...X(26), Y(0)...Y(26)             JOW08025
           VECTOR VALUES TABLE = $(8F10.5)*$                         JOW08026
START      READ FORMAT IN, DELT, EPSMAX, N                           JOW08030
           VECTOR VALUES IN = $2F10.5,I10*$                          JOW08040
           PRINT COMMENT $1      UNSTEADY STATE HEAT CONDUCTION IN SOLIDJOW08041
          1IFYING INGOT WITH THE PARAMETERS$                         JOW08042
           PRINT RESULTS DELT, EPSMAX, N                             JOW08045
           B = (540.0/10.1)*(2.0/N)*(2.0/N)/DELT                     JOW08050
           HEURE = 0.0                                               JOW08055
           T(0) = 150.0                                              JOW08060
           S(0) = 150.0                                              JOW08070
           THROUGH ONE, FOR I = 1, 1, I.G.N                          JOW08080
ONE        T(I) = 400.0                                              JOW08090
BEGIN      THROUGH THREE, FOR I = 1, 1, I.G.N                        JOW08100
           S(I) = T(I)                                               JOW08110
TWO        THROUGH TWO, FOR J = 0, 1, Y(J).G.S(I)                    JOW08120
```

MAD Program and Data (continued)

```
          A = X(J-1) + (X(J)-X(J-1))*(S(I)-Y(J-1))/(Y(J)-Y(J-1))          JOW08130
THREE     GAM(I) = B*(0.038 + A*12.0)                                     JOW08140
          EPS = 10.0                                                      JOW08150
          THROUGH FIVE, FOR K = 1, 1, EPS.L.EPSMAX                        JOW08160
          EPS = 0.0                                                       JOW08170
          THROUGH FOUR, FOR I = 1, 1, I.G.N-1                             JOW08180
          DUM = T(I)                                                      JOW08190
          T(I) = (T(I+1) + T(I-1) + GAM(I)*S(I))/(GAM(I) + 2.0)           JOW08200
FOUR      EPS = EPS + .ABS.(T(I) - DUM)                                   JOW08210
          DUM = T(N)                                                      JOW08220
          T(N) = (2.0*T(N-1) + GAM(N)*S(N))/(GAM(N) + 2.0)                JOW08230
FIVE      EPS = EPS + .ABS.(T(N) - DUM)                                   JOW08240
          HEURE = HEURE + DELT                                            JOW08245
          PRINT FORMAT OUT, HEURE, K, T(0)...T(N)                         JOW08250
          VECTOR VALUES OUT = $S10,F10.5,I10/(S5,11F8.3)*$                JOW08260
          WHENEVER T(N).G.200.0, TRANSFER TO BEGIN                        JOW08270
          TRANSFER TO START                                               JOW08280
          END OF PROGRAM                                                  JOW08290
$ DATA
  0.0119    0.  102    0.00874   0.  756   0.00657   .00575   0.00509   0.00454
  0.00412   0.  375    0.00341   0.  315   0.00291   .00270   0.00252   0.00238
  0.00223   0.  211    0.00200   0.  190   0.00181   .00173   0.00167   0.00160
  0.00153   0.  147    0.00140 150.      160.0     170.0     180.0     190.0
200.0     210.       220.0     230.      240.0     250.0     260.0     270.0
280.0     290.       300.0     310.      320.0     330.0     340.0     350.0
360.0     370.       380.0     390.      400.0     410.0
  4.0       0.2              20
```

Computer Output

A typical set of results obtained using the data shown with the MAD Program above is presented below.

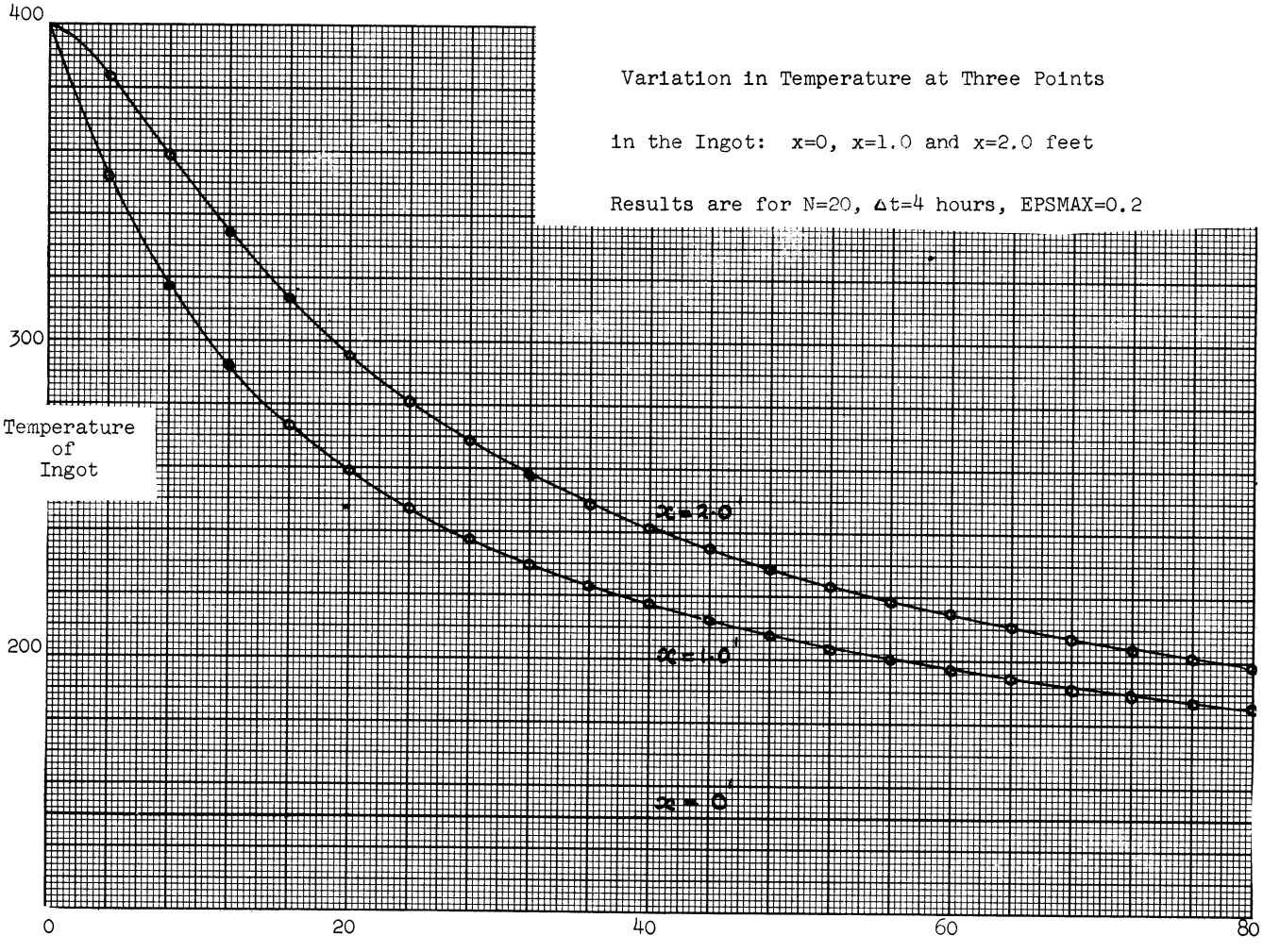
```
UNSTEADY STATE HEAT CONDUCTION IN SOLIDIFYING INGOT WITH THE PARAMETERS

      DELT =     4.000000,        EPSMAX =      .200000,          N =          20
        4.00000          137
150.000 188.633 221.611 249.273 272.611 292.291 308.877 322.843 334.588 344.449 352.707
359.598 365.319 370.034 373.677 376.959 379.367 381.170 382.421 383.154 383.392
        8.00000          119
150.000 174.429 197.230 218.172 237.230 254.483 270.028 283.968 296.405 307.441 317.175
325.697 333.093 339.434 344.786 349.210 352.757 355.470 357.382 358.517 358.889
       12.00000          105
150.000 168.875 186.987 204.062 220.010 234.862 248.448 260.970 272.397 282.756 292.081
300.464 307.755 314.163 319.657 324.266 327.995 330.878 332.925 334.146 334.547
       16.00000           93
150.000 165.706 180.942 195.478 209.213 222.101 234.116 245.254 255.516 264.909 273.441
281.122 287.959 293.962 299.143 303.509 307.068 309.827 311.791 312.965 313.351
       20.00000           85
150.000 163.552 176.768 189.461 201.528 212.918 223.600 233.552 242.766 251.238 258.965
265.948 272.190 277.691 282.452 286.473 289.757 292.307 294.125 295.212 295.569
       24.00000           75
150.000 161.943 173.626 184.890 195.642 205.827 215.408 224.365 232.680 240.342 247.349
253.694 259.373 264.385 268.729 272.405 275.411 277.749 279.418 280.416 280.744
       28.00000           67
150.000 160.674 171.138 181.255 190.937 200.129 208.797 216.915 224.467 231.438 237.816
243.604 248.789 253.370 257.341 260.704 263.454 265.592 267.117 268.029 268.328
       32.00000           61
150.000 159.636 169.097 178.263 187.054 195.415 203.313 210.721 217.622 224.000 229.844
235.147 239.901 244.105 247.753 250.842 253.371 255.337 256.739 257.577 257.852
       36.00000           56
150.000 158.769 167.388 175.753 183.790 191.445 198.685 205.483 211.822 217.687 223.067
227.952 232.335 236.209 239.572 242.421 244.754 246.569 247.864 248.638 248.891
       40.00000           52
150.000 158.030 165.932 173.611 180.998 188.045 194.716 200.988 206.840 212.259 217.234
221.754 225.812 229.402 232.518 235.158 237.318 238.998 240.196 240.911 241.145
       44.00000           48
150.000 157.394 164.675 171.759 178.583 185.100 191.278 197.089 202.517 207.546 212.164
216.364 220.137 223.476 226.377 228.835 230.847 232.412 233.528 234.195 234.412
       48.00000           45
150.000 156.838 163.577 170.141 176.471 182.523 188.265 193.672 198.725 203.410 207.714
211.629 215.148 218.264 220.973 223.269 225.150 226.613 227.656 228.280 228.483
```

Computer Output (continued)

```
        52.00000          43
 150.000 156.349 162.610 168.713 174.665 180.245 185.600 190.647 195.366 199.745 203.769
 207.431 210.723 213.638 216.173 218.323 220.085 221.455 222.433 223.017 223.208
        56.00000          42
 150.000 155.916 161.752 167.446 172.949 178.221 183.231 187.957 192.380 196.484 200.259
 203.695 206.784 209.521 211.899 213.916 215.569 216.855 217.773 218.321 218.500
        60.00000          36
 150.000 155.529 160.986 166.314 171.466 176.409 181.110 185.547 189.702 193.560 197.110
 200.342 203.249 205.825 208.064 209.964 211.519 212.729 213.592 214.108 214.275
        64.00000          36
 150.000 155.161 160.298 165.297 170.135 174.780 179.201 183.377 187.290 190.925 194.272
 197.320 200.063 202.494 204.607 206.399 207.868 209.010 209.825 210.312 210.470
        68.00000          34
 150.000 154.868 159.677 164.378 168.932 173.307 177.474 181.414 185.108 188.541 191.704
 194.585 197.178 199.477 201.477 203.172 204.562 205.642 206.412 206.872 207.021
        72.00000          33
 150.000 154.583 159.112 163.543 167.838 171.966 175.902 179.625 183.118 186.367 189.361
 192.090 194.546 196.724 198.619 200.227 201.544 202.569 203.306 203.756 203.877
        76.00000          31
 150.000 154.325 158.600 162.784 166.842 170.746 174.471 177.996 181.306 184.386 187.226
 189.815 192.147 194.215 196.014 197.540 198.792 199.765 200.459 200.873 201.007
        80.00000          30
 150.000 154.088 158.130 162.089 165.930 169.628 173.158 176.502 179.643 182.567 185.265
 187.725 189.942 191.908 193.619 195.071 196.260 197.185 197.845 198.239 198.366
```

Discussion of Results

In order to investigate the effect of choice of grid spacing, time increment and allowable error on the computed temperatures, the program was run for several different selections of N, Δt and ϵ_{max}. The output printed above corresponds to one such choice, viz N=20, Δt = 4.0 hours, and ϵ_{max} = 0.20, and the resulting temperatures at x = 0,1 and 2 feet are plotted against time in the figure below. The results for the remaining runs are summarized in the table below.



Example Problem No. 93

Effect of choice of N, Δt, and ε_{max} on the time t (hours) for the face x=2.0 feet to cool to 200°F

Effect of time increment (For N=20, ε_{max}=0.2)

Δt	t
4.0	77.52
2.0	76.97
1.0	76.66
0.5	76.42
0.25	76.07
0.1	75.90

Effect of allowable Error (N=20, Δt=1.0)

ε_{max}	t
1.0	84.73
0.5	79.49
0.2	76.66
0.1	75.80
0.05	75.30
0.02	75.06
0.01	74.98

Effect of grid spacing (Δt=1.0, ε_{max}=0.2)

N	t
5	75.21
10	75.50
20	76.66
30	77.97

It is seen from the table that there is, perhaps, not so much need to make Δt small as to ensure, by reducing ε_{max}, that the sequence of iterations has converged sufficiently at each time step. The average numbers of iterations required for ε_{max} values of 1.0, 0.1 and 0.01 were 16, 28 and 41 respectively. The IBM 709 computer performed approximately 20 such iterations (over 20 grid points) per second. The slight divergence of t as N is increased has not been explained.

Critique

Although the present example, together with some notes on finite difference methods, was assigned at the start of the semester, many students waited until the 11th week, when heat transfer was first discussed in lectures, to start work on the problem. Half the class succeeded in obtaining correct answers to what amounted to a fairly difficult problem at the Junior level.

The problem well illustrated the ability of the computer to handle an otherwise formidable task.

Example Problem No. 94

COOLING OF PIG IRON IN A TRANSFER LADLE

by

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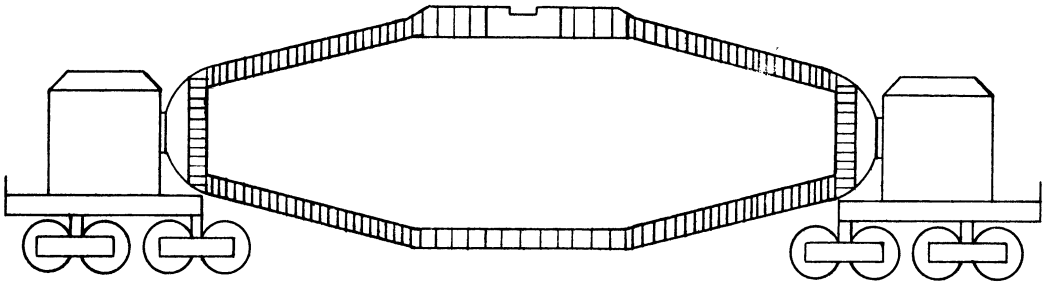
The University of Michigan

Course: Rate Operations Credit Hours: 5 Level: Junior

The pig iron produced in an iron blast furnace is transferred to steelmaking facilities in a ladle mounted on a railroad car. Several types of ladles are used, the most prominent one being the Pugh-type which is a cigar-shaped tilting ladle. The pig iron is tapped from the blast furnace into the ladle and then transferred to the steelmaking facilities which may be some distance from the blast furnace plant. It is of interest then to know the time which one can allow the metal to remain in the ladle without any solidification taking place.

Statement of Problem

Write and test a MAD program which will permit a calculation of the temperature drop of liquid pig iron held in a closed transport ladle of the Pugh-type (See Figure 1). Using the test data, carry the computations to either the initial solidification temperature or to an elapsed time of twenty-four hours.



150 Ton BOTTLE CAR

Figure 1.

Suggested Approach: Assume the following:

1. The temperature of the liquid metal is uniform and equal to the internal interface temperature of the refractory lining of the ladle car.
2. The heat losses may be estimated by determining the rate of loss over short intervals of time and approximating the heat loss as the rate-time product.
3. Neglect the thermal resistance of the thin steel shell which surrounds the ladle.

Problem Preparation: Do the following in the given order:

1. Prepare a flow diagram for the problem in the form of concise algorithmic statements.
2. Convert the flow diagram to a set of MAD statements.
3. Keypunch the statements and required data cards.
4. Flow diagram, MAD statements, and keypunched cards should be submitted.

Data and Nomenclature: The program should be tested on a ladle car used for pig iron transport under the following conditions:

TM	Temperature of charged metal, 2700°F
TA	Temperature of surroundings, 80°F
AO	Area of external surface, 800 ft^2
AI	Area of internal surface, 530 ft^2
K	Thermal conductivity of refractory, 2.35 BTU-ft/hr-ft^2-°R
L	Thickness of refractory, 1.5 ft
HC	Convective heat transfer coefficient, 0.28 BTU/$°R^{0.25}$
E	Emissivity of steel shell, 0.8
W	Weight of metal charged, 150 tons
F	Factor to account for specific heat of ladle, 1.4
EPS	Tolerable error in surfact temperature, 0.1 °R
I	Time interval, 0.5 hour
J	Number of time intervals
IMAX	Maximum time of holding, 24 hours
NMAX	Maximum number of iterations to determine surface temperature, 100
TLOW	Temperature of initial solidification, 2100°F
CP	Specific heat of metal, 0.2 BTU/lb °R
R	Radiation from surroundings to the ladle
AM	Log mean area for heat transfer through the refractory
CPM	Gross heat capacity for ladle and metal, BTU/lb °F
TO	Temperature of metal at time, P, °R
P	Elapsed time from charging of ladle, hours
TS	Temperature of outside surface, °R
N	Number of iterations required for temperature convergence
QC	Conduction heat transfer, BTU/hr
QR	Radiation and convection heat transfer, BTU/hr
TI	Most recent value of TS during iteration, °R
TN	Metal temperature after iteration, i.e., latest TO, °R
TX	TN in °F
TY	TI in °F

Solution

Heat is transferred to the surroundings by conduction through the refractory and then by radiation and convection to the ambient surroundings at temperature TA. The conduction heat transfer during a unit time is

$$QC = \frac{K \cdot AM}{L} \quad (TO-TI)$$

where the cylindrical wall is being considered; the area for heat conduction is given by the relationship

$$AM = \frac{AO-AI}{\ln \frac{AO}{AI}}$$

The radiation loss during unit time is

$$Q_r = 0.173 \times 10^{-8} \ (E) \ (TI^4-TA^4) AO$$

The convection loss is

$$Q_c = h \ AO \ (TI-TA)$$

Here the convection coefficient h is a function of the temperature difference to the one-quarter power, $(TI-TA)^{0.25}$. Therefore, one may write

$$Q_c = HC \cdot AO\ (TI-TA)^{1.25}$$

The combined convection and radiation loss is

$$QR = Q_r + Q_c$$

The heat loss from the metal results in a decrease in its temperature. This decrease in energy is

$$\Delta E = 2000\ W \cdot CP \cdot F\ (TO-TN)$$

By energy balance

$$QC = QR$$

If either of these is multiplied by the time interval, I (it must be short enough so that the changes in the temperature during the interval are small), a quantity of heat is obtained which determines the decrease in metal temperature during the interval. Thus,

$$I \cdot QC = 2000\ W \cdot CP \cdot F\ (TO-TN) = CPM\ (TO-TN)$$

where CPM is the combination of a number of constants.

At the start of any time interval the metal temperature TO and the ambient temperature TA are known. The surface temperature TI is notknown, so a first guess is made. This allows a QC and QR to be calculated. If TI has been guessed correctly, QC comes out equal to QR, and then the temperature of the metal at the end of the short time interval may be calculated as

$$TN = TO - \frac{I \cdot QC}{CPM}$$

If TI has not been determined within $0.1^{\circ}R$, it is necessary to correct the assumed temperature. The magnitude of the change to be made in TI depends upon how different QC and QR turn out to be for a given TI. In this solution it was decided that if

$$|TS - TI| \geqslant EPS$$

where EPS is $0.1^{\circ}R$, the surface temperature would be changed to

$$TI = TI + (100) \cdot \left(\frac{QC-QR}{QR}\right)$$

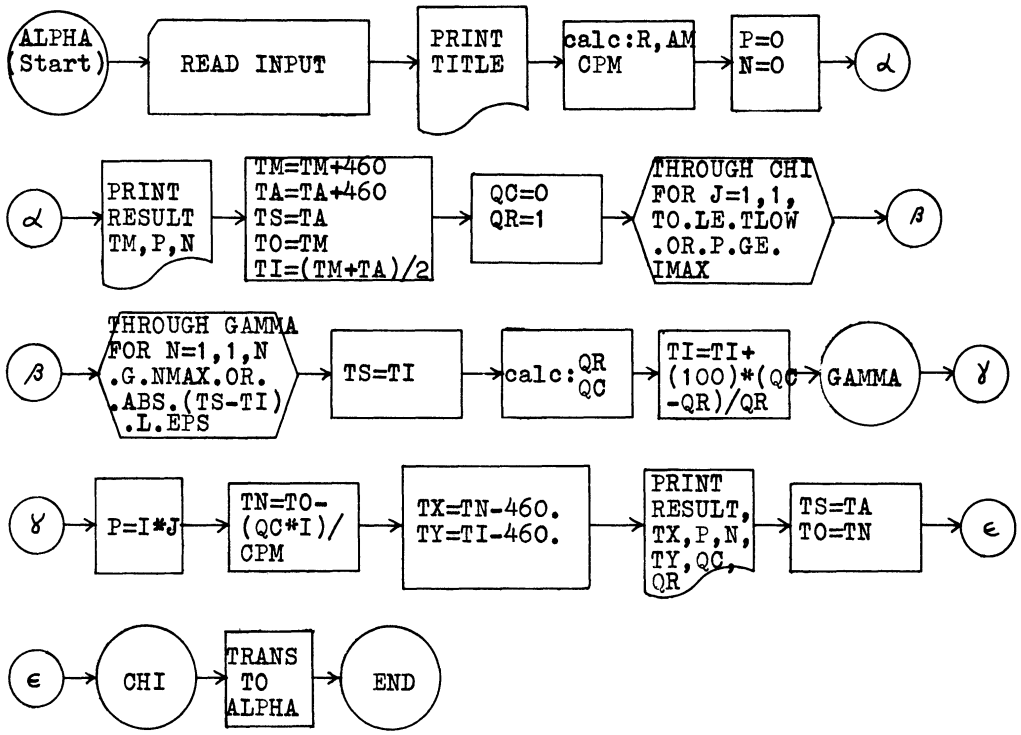
It is clear that a higher order approximation might be made in the heat transfer equations by putting in the average metal or average surface temperatures during the time interval. Thus, for conduction, one might write

$$QC = \frac{K \cdot AM}{L}\left(\frac{TO+TN}{2} - TI_{ave}\right)$$

The anticipated change in temperature, however, did not merit this refinement, so it was simply assumed for the heat transfer calculations that TO and TI remained constant during the short time interval.

Flow Diagram

Cooling of Liquid-Metal Transport Ladle



MAD Program and Data

```
$COMPILE MAD, EXECUTE,DUMP
 ALPHA     READ  FORMAT INPUT, TM, TA, AI, AO, K, L, HC, E, W, CP,          1
          2F, EPS, I, IMAX, NMAX, TLOW                                      2
           PRINT FORMAT TITLE1, TM, TA, AI, AO, K, L, HC, E, W, CP          3
           PRINT FORMAT TITLE2, F, EPS, I, IMAX, NMAX, TLOW                 4
           R =  (0.173E-8)*E*(TA.P.4)                                       5
           AM = (AO-AI)/(+ELOG.(AO/AI))                                     6
           CPM = W*2000.*CP*F                                               7
           P = 0                                                            8
           N = 0                                                            9
           PRINT FORMAT RESULT, TM, P, N                                   10
           TM = TM + 460.                                                  11
           TA = TA+ 460.                                                   12
           TS = TA                                                         13
           TO = TM                                                         14
           TI = (TM+TA)/2                                                  15
           QC = 0.0                                                        16
           QR = 1.0                                                        17
           THROUGH CHI, FOR J=1,1, TO.LE.(TLOW+460.).OR.P.GE.IMAX          18
           THROUGH GAMMA, FOR N=1,1, N.G.NMAX.OR..ABS.(TS-TI).L.EPS        19
           TS = TI                                                         20
           QR= AO*(HC*((TI-TA).P.(1.25))+(0.173E-8)*E*(TI.P.4)-R)          21
           QC = K*AM*(TO-TI)/L                                             22
 GAMMA     TI = TI + (100)*(QC -QR)/QR                                     23
           P = I*J                                                         24
           TN = TO -(QC*I)/CPM                                             25
           TX = TN - 460.                                                  26
           TY = TI - 460.                                                  27
           PRINT FORMAT RESULT, TX, P, N, TY, QC, QR                       28
           TS = TA                                                         29
 CHI       TO = TN                                                         30
           INTEGER J, N, NMAX                                              31
           TRANSFER TO ALPHA                                               32
           VECTOR VALUES INPUT = $4F5.0,4F5.2,F4.0,4F4.2,F4.0,I3,F5.0*$    33
```

MAD Program and Data, Continued

```
 VECTOR VALUES TITLE1= $48H1TEMPERATURE DROP OF LIQUID METAL I   34
2N A LADLE CAR //5H DATA/34H INITIAL METAL TEMPERATURE F, TM =   35
3F7.1/  25H AIR TEMPERATURE F, TA = F6.1/25H INSIDE AREA SQ FT  36
4, AI = F5.1/ 26H OUTSIDE AREA SQ FT, AO = F5.1/ 27H THERMAL C  37
5ONDUCTIVITY, K = F4.1/ 30H REFRACTORY THICKNESS FT, L = F4.1/  38
630H CONVECTION COEFFICIENT, HC  =    F4.1/ 23H SHELL EMISSIVI  39
7TY, E =       F4.1/ 24H METAL WEIGHT TONS, W =  F5.1/ 34H SPE  40
8CIFIC HEAT METAL BTU/LB, CP = F4.1*$                           41
 VECTOR VALUES TITLE2 = $18H HEAT FACTOR, F = F4.1/ 32H TEMPER  42
2ATURE DEVIATION F, EPS = F4.2/24H TIME INCREMENT HR, I = F4.1  43
3/ 37H MAXIMUM NUMBER OF INCREMENTS, IMAX = F5.1/ 34H MAXIMUM   44
4NUMBER OF TRIALS, NMAX = I4/ 26H FREEZING POINT F, TLOW = F6.  45
51//// 30H METAL TEMPERATURE VERSUS TIME ///7H  METAL,S5,4HTIM  46
6E,S4,10HITERATIONS,S4,7HSURFACE,S4,10HCONDUCTION,S4,8HRAD-CON  47
7V/8H  TEMP F,S5,2HHR,S19,6HTEMP F,S4,11HLOSS BTU/HR,S3,11HLOS  48
8S BTU/HR//*$                                                   49
 VECTOR VALUES RESULT = $S1,F8.2,F6.1,I11,F14.2,F14.2,F13.2*$   50
 END OF PROGRAM                                                 51
$DATA
 2700    80  530  800  240  150   30   80 150  18 140  10  50  48100 2100  D-1
```

Computer Output

```
TEMPERATURE DROP OF LIQUID METAL IN A LADLE CAR

DATA
INITIAL METAL TEMPERATURE F, TM = 2700.0
AIR TEMPERATURE F, TA =   80.0
INSIDE AREA SQ FT, AI = 530.0
OUTSIDE AREA SQ FT, AO = 800.0
THERMAL CONDUCTIVITY, K =  2.4
REFRACTORY THICKNESS FT, L =  1.5
CONVECTION COEFFICIENT, HC  =  .3
SHELL EMISSIVITY, E =   .8
METAL WEIGHT TONS, W = 150.0
SPECIFIC HEAT METAL BTU/LB, CP =   .2
HEAT FACTOR, F =  1.4
TEMPERATURE DEVIATION F, EPS =  .10
TIME INCREMENT HR, I =   .5
MAXIMUM NUMBER OF INCREMENTS, IMAX = 48.0
MAXIMUM NUMBER OF TRIALS, NMAX =  100
FREEZING POINT F, TLOW = 2100.0


METAL TEMPERATURE VERSUS TIME

 METAL      TIME     ITERATIONS     SURFACE     CONDUCTION     RAD-CONV
 TEMP F      HR                    TEMP F     LOSS BTU/HR    LOSS BTU/HR

 2700.00     .0          0
 2685.61     .5         25         626.47     2175488.53     2177499.22
 2671.31    1.0          7         624.59     2162391.78     2163937.19
 2657.10    1.5          7         622.74     2149327.75     2150826.00
 2642.97    2.0          7         620.90     2136346.56     2137822.84
 2628.92    2.5          7         619.06     2123450.69     2124906.56
 2614.96    3.0          7         617.22     2110639.69     2112075.47
 2601.09    3.5          7         615.40     2097913.03     2099328.97
 2587.30    4.0          7         613.57     2085270.08     2086666.47
 2573.59    4.5          7         611.75     2072710.31     2074087.20
 2559.96    5.0          7         609.93     2060233.08     2061590.89
 2546.42    5.5          7         608.12     2047837.87     2049176.80
```

Computer Output, Continued

2532.96	6.0	7	606.32	2035524.12	2036844.19
2519.57	6.5	7	604.51	2023291.25	2024592.89
2506.27	7.0	7	602.71	2011138.69	2012422.09
2493.05	7.5	7	600.92	1999065.89	2000331.17
2479.91	8.0	7	599.13	1987072.33	1988319.81
2466.85	8.5	7	597.34	1975157.45	1976387.30
2453.86	9.0	7	595.56	1963320.70	1964533.14
2440.95	9.5	7	593.79	1951561.56	1952756.69
2428.12	10.0	7	592.01	1939879.47	1941057.56
2415.37	10.5	6	590.31	1928169.75	1930086.48
2402.69	11.0	7	588.48	1916739.84	1917921.75
2390.09	11.5	6	586.78	1905187.78	1907058.81
2377.57	12.0	7	584.97	1893907.50	1895055.41
2365.12	12.5	6	583.27	1882506.14	1884329.44
2352.74	13.0	6	581.53	1871269.09	1873123.59
2340.44	13.5	6	579.79	1860112.70	1861947.16
2328.21	14.0	6	578.05	1849029.78	1850840.55
2316.05	14.5	6	576.32	1838019.33	1839806.17
2303.97	15.0	6	574.59	1827080.78	1828844.14
2291.96	15.5	6	572.86	1816213.64	1817953.58
2280.02	16.0	6	571.14	1805417.45	1807134.25
2268.15	16.5	6	569.42	1794691.66	1796385.69
2256.35	17.0	6	567.71	1784035.87	1785707.27
2244.62	17.5	6	566.00	1773449.53	1775098.58
2232.96	18.0	6	564.29	1762932.20	1764559.14
2221.37	18.5	6	562.59	1752483.39	1754088.47
2209.85	19.0	6	560.90	1742102.62	1743686.16
2198.39	19.5	6	559.21	1731789.44	1733351.67
2187.01	20.0	6	557.52	1721543.39	1723084.47
2175.69	20.5	6	555.84	1711364.00	1712884.09
2164.44	21.0	6	554.16	1701250.78	1702750.19
2153.25	21.5	6	552.48	1691203.34	1692682.25
2142.13	22.0	6	550.81	1681221.19	1682679.97
2131.08	22.5	6	549.14	1671303.89	1672742.67
2120.09	23.0	6	547.48	1661450.97	1662869.97
2109.17	23.5	6	545.82	1651662.03	1653061.48
2098.31	24.0	6	544.17	1641936.62	1643316.69

Discussion of Results

The result of the calculation is in keeping with observations from steel mill operations, i.e., pig iron can be allowed to remain in a bottle car for periods ranging up to twenty-four hours.

Critique

This problem has not been used in teaching but appears to be well suited for illustrating the use of the computer in solving heat transfer problems of the type which commonly arise in equipment design. An extension of the problem is possible in terms of the cost of refractories which could be used as lining and insulating materials for the ladle.

Example Problem No. 95

DIGITAL COMPUTER ANALYSIS OF HEAT FLOW AND TEMPERATURE DISTRIBUTION AROUND A COPPER CONVERTER TUYERE[1]

by

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Course: Rate Operations Credit Hours: 5 Level: Junior

Statement of Problem

Write and test a MAD program which will perform the relaxation calculations outlined by Krivsky and Schuhmann[1] for determining the heat flow and temperature distribution around a copper converter tuyere.

The cross-section of a copper converter through a tuyere center line is shown schematically in Figure 1. A relaxation technique was employed to obtain a solution and involved dividing the solid into equally-spaced grid points, specifying the boundary conditions, and assuming a steady state temperature distribution which dictates that the heat flow into each grid point shall be zero. The heat flow is idealized into a two-dimensional matrix with radial symmetry about the center line of the tuyere through which the blast air is supplied. The reference paper derives the equations for heat flow into each type of grid point which includes the interior points, interior or exterior surface points, tuyere surface points, and the points at the tuyere source and tuyere mouth. These heat flow equations are then solved in terms of the steady state temperature of the grid point itself and set into a series of conditional statements which permits the calculation of the steady state temperature at each grid point as a function of the temperature of the surrounding grid points or boundary temperatures. (It should be noted that in Figure 6 of the reference, the equation which reads

$$Q_{4\rightarrow 0} = h_4 \pi (r + \frac{\Delta r}{4}) \ (T_4 - T_0)$$

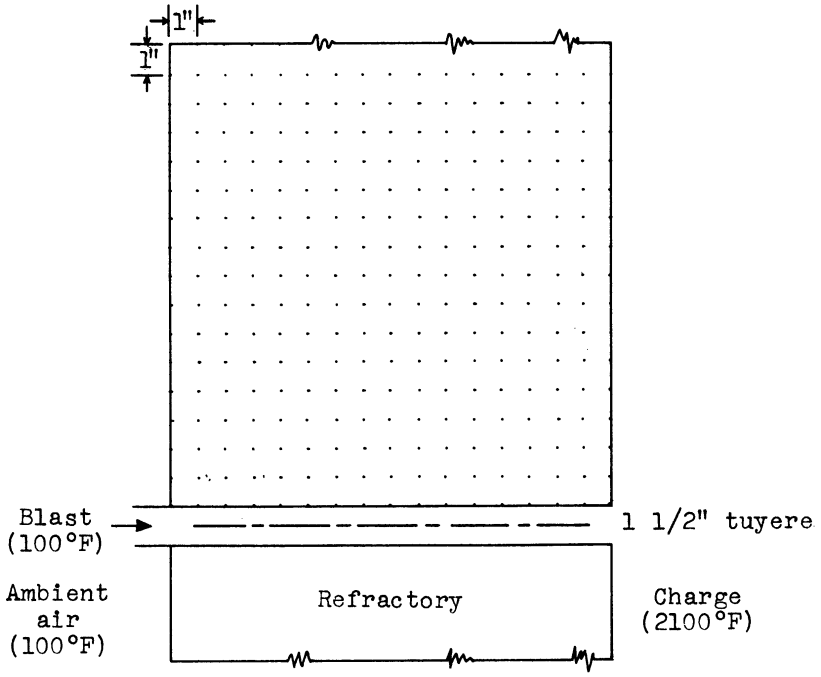
should read

$$Q_{4\rightarrow 0} = h_4 \ \Delta r \pi (r + \frac{\Delta r}{4}) \ (T_4 - T_0).$$

---

[1] Krivsky, W. A., and R. Schuhmann, Jr. "Heat Flow and Temperature Distribution Around a Copper Converter Tuyere," AIME Transactions, 215, February 1959, p. 82.

Figure 1.



Idealized cross section of single 1 1/2 in. tuyere in 15 in. wall, showing grid of points for relaxation calculation.[1]

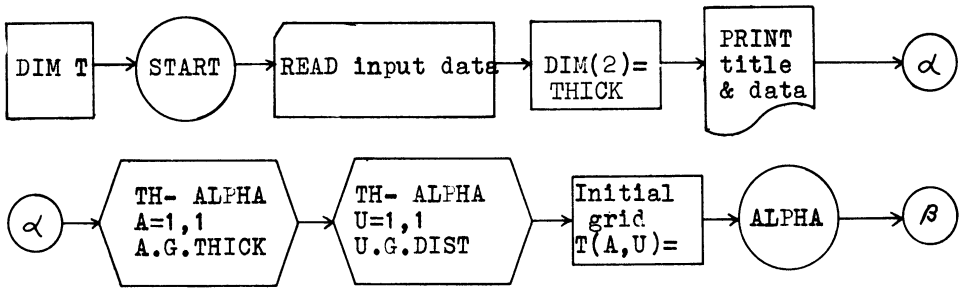
The Basic Approach:

a. Initialize the temperature distribution by a programmed estimate of the temperature at each grid point.

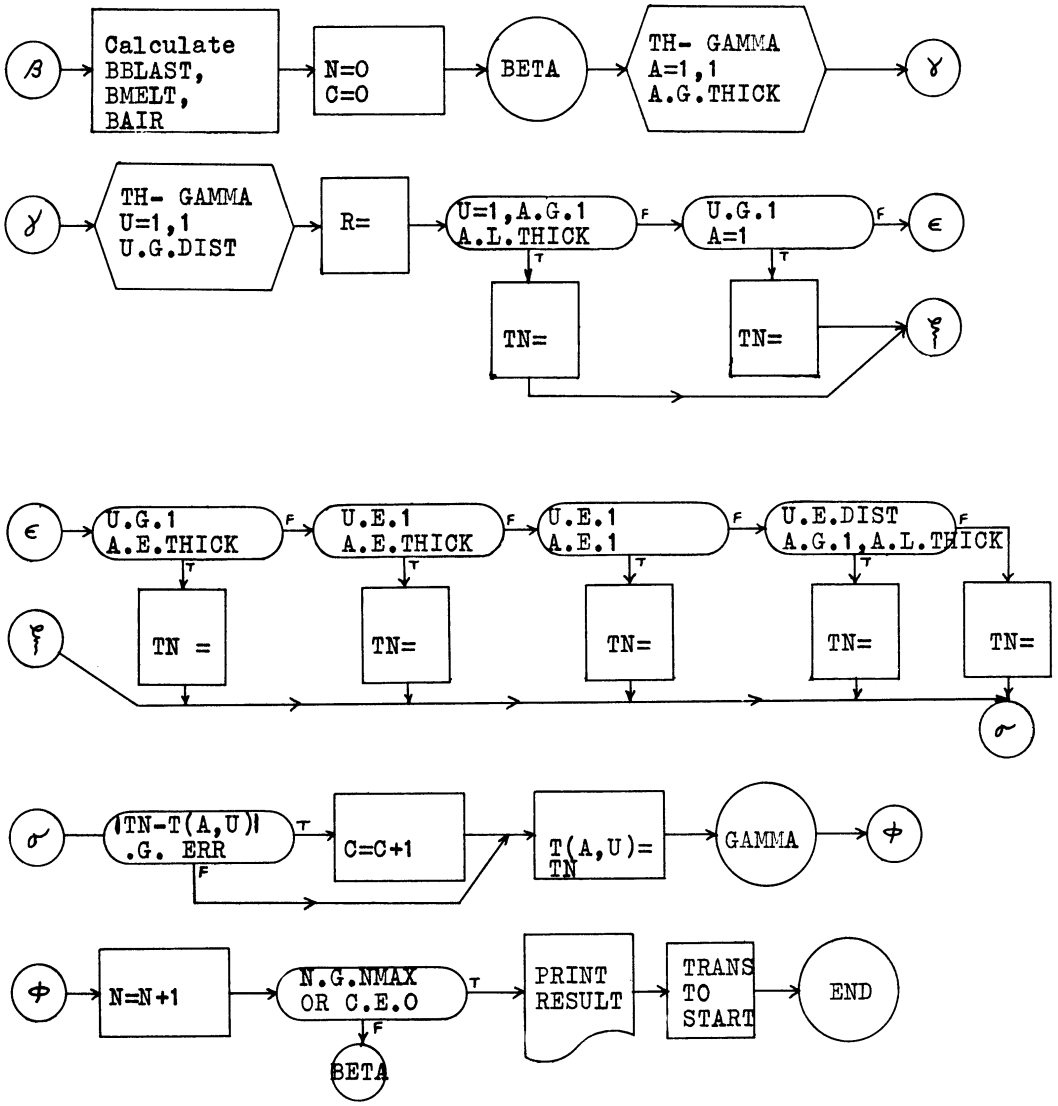
b. Make a point by point calculation of the steady state temperature by systematically moving through the grid, utilizing the surrounding temperatures and heat flow equations of each grid point.

c. After calculating the temperature at each grid point, make a comparison of the calculated temperature with the temperature which existed on the previous pass through the grid. When there are no temperature adjustments which are greater than a specified temperature increment ϵ for any of the points in the grid from one pass to the next, the calculation is considered complete and the temperature distribution is then printed out.

Flow Diagram



Flow Diagram, Continued



MAD Program and Data

```
$COMPILE MAD, EXECUTE, PUNCH OBJECT, PUNCH LIBRARY, DUMP          TUYER
            DIMENSION T(3800,DIM)                                          0
            VECTOR VALUES DIM = 2, 1, 0                                   00
 START      READ FORMAT INPUT, DIST, THICK, NMAX, SCALE, RADIUS, TMELT,    1
           2TBLAST, TAIR, HBLAST, HMELT, HAIR, KCOND, ERR                  2
            VECTOR VALUES INPUT = $3I5,F5.3,F6.4,7F6.2,F4.2*$              3
            DIM(2) = THICK                                                00
            PRINT FORMAT TITLE                                             4
            VECTOR VALUES TITLE = $58H1TEMPERATURE DISTRIBUTION AROUND A    5
           2COPPER CONVERTER TUYERE///*$                                   6
            PRINT FORMAT LIST,  DIST, THICK, NMAX, SCALE, RADIUS, TMELT,    7
           2TBLAST, TAIR, HBLAST, HMELT, HAIR, KCOND, ERR                  8
            VECTOR VALUES LIST =$5H DATA//33H DISTANCE FROM TUYERE IN SPA   9
           1CES = I4/ 33H REFRACTORY THICKNESS IN SPACES = I4/ 31H MAXIMU  10
           2M NUMBER OF ITERATIONS = I4/ 27H SCALE IN SPACES PER FOOT =F6  11
           3,3/26H TUYERE RADIUS IN FEET =   F5.4/ 41H MELT TEMPERATURE I  12
           4N DEGREES FAHRENHEIT = F5.0/ 42H BLAST TEMPERATURE IN DEGREES  13
           5 FAHRENHEIT = F5.0/40H AIR TEMPERATURE IN DEGREES FAHRENHEIT   14
           6=  F5.0/ 29H HBLAST, BTU PER HR-SQ FT-F = F5.1/ 28H HMELT, BT  15
           7U PER HR-SQ FT-F = F5.1/ 27H HAIR, BTU PER HR-SQ FT-F = F5.1/  16
```

MAD Program and Data, Continued

```
            860H THERMAL CONDUCTIVITY OF REFRACTORY, BTU-FT PER HR-SQ FT-F  17
            9 = F5.1/ 21H ERROR IN DEGREES F = F4.2///*$                   18
             THROUGH ALPHA, FOR A=1,1, A.G.THICK                           19
             THROUGH ALPHA, FOR U=1,1, U.G.DIST                            20
ALPHA        T(A,U) = TAIR + (TMELT - TAIR)*(A-1)/(THICK-1)                21
             BBLAST = (HBLAST)/(KCOND*SCALE)                               22
             BMELT = (HMELT)/(KCOND*SCALE)                                 23
             BAIR = (HAIR)/(KCOND*SCALE)                                   24
             N = 0                                                         25
BETA         C = 0                                                         26
             THROUGH GAMMA, FOR A = 1,1, A.G.THICK                         27
             THROUGH GAMMA, FOR U = 1,1, U.G.DIST                          28
             R = RADIUS + (U-1)/SCALE                                      29
             WHENEVER U.E.1.AND.A.G.1.AND.A.L.THICK                        30
             TN = ((2*BBLAST*TBLAST)+(1+(1/(4*R*SCALE)))*(T(A-1,U)+T(A+1,U 31
            2)+(2*T(A,U+1))))/(2*BBLAST+4+(1/(R*SCALE)))                   32
             OR WHENEVER U.G.1.AND.A.E.1                                   33
             TN= (T(A,U-1)+T(A,U+1)+(2*T(A+1,U))+(2*BAIR*TAIR)+((T(A,U+1)- 34
            2T(A,U-1))*(1/(2*R*SCALE))))/(4+(2*BAIR))                      35
             OR WHENEVER U.G.1.AND.A.E.THICK                               36
             TN = (T(A,U-1)+T(A,U+1)+(2*T(A-1,U))+(2*BMELT*TMELT)+(T(A,U+1 37
            2)-T(A,U-1))*(1/(2*R*SCALE)))/(4+(2*BMELT))                    38
             OR WHENEVER U.E.1.AND.A.E.THICK                               39
             TN =((BBLAST*TBLAST)+(T(A-1,U)*(1+(1/(4*R*SCALE))))+(T(A,U+1) 40
            2*(1+(1/(2*R*SCALE))))+(TMELT*BMELT*(1+(1/(4*R*SCALE)))))/(2+B 41
            3BLAST+(1/(4*R*SCALE))+(1/(2*R*SCALE))+((BMELT)*(1+(1/(4*R*SCA 42
            4LE))))                                                        43
             OR WHENEVER U.E.1.AND.A.E.1                                   44
             TN =((BBLAST*TBLAST)+(T(A+1,U)*(1+(1/(4*R*SCALE))))+(T(A,U+1) 45
            2*(1+(1/(2*R*SCALE))))+(TAIR*BAIR*(SCALE+(1/(4*R)))))/(2+BBLAS 46
            3T+(1/(4*R*SCALE))+(1/(2*R*SCALE))+(BAIR*(SCALE+(1/(4*R)))))   47
             OR WHENEVER U.E.DIST.AND.A.G.1.AND.A.L.THICK                  48
             TN = T(1,DIST) + ((T(THICK,DIST)-T(1,DIST))*(A-1)/(THICK-1))  49
             OTHERWISE                                                     50
             TN = (T(A-1,U)+T(A+1,U)+T(A,U+1)+T(A,U-1)+((T(A,U+1)-T(A,U-1) 51
            2)/(2*R*SCALE)))/4                                             52
             END OF CONDITIONAL                                            53
             WHENEVER.ABS.(TN-T(A,U)).G.ERR, C = C+1                       54
GAMMA        T(A,U) = TN                                                   55
             N = N+1                                                       56
             WHENEVER .NOT. (N.G.NMAX.OR.C.E.0), TRANSFER TO BETA          57
             PRINT FORMAT RESULT, N, C, T(1,1)...T(THICK,DIST)             58
             TRANSFER TO START                                             59
             INTEGER A, U, THICK, DIST, NMAX, C, N                         60
             VECTOR VALUES RESULT = $4H N =I4, 4H C =I4/(10F10.2)*$        61
             END OF PROGRAM                                                62
$DATA
   16   16  10012000  0625210000 10000 10000 20000 50000   600   200  50  D-9
   16   16  10012000  0625210000 10000 10000  1000 50000   600   200  50  D-10
```

Computer Output

```
TEMPERATURE DISTRIBUTION AROUND A COPPER CONVERTER TUYERE

DATA

DISTANCE FROM TUYERE IN SPACES =  16
REFRACTORY THICKNESS IN SPACES =  16
MAXIMUM NUMBER OF ITERATIONS = 100
SCALE IN SPACES PER FOOT =12.000
TUYERE RADIUS IN FEET =  .0625
MELT TEMPERATURE IN DEGREES FAHRENHEIT = 2100
BLAST TEMPERATURE IN DEGREES FAHRENHEIT =  100
AIR TEMPERATURE IN DEGREES FAHRENHEIT =  100
HBLAST, BTU PER HR-SQ FT-F =200.0
HMELT, BTU PER HR-SQ FT-F =500.0
HAIR, BTU PER HR-SQ FT-F =  6.0
THERMAL CONDUCTIVITY OF REFRACTORY, BTU-FT PER HR-SQ FT-F =  2.0
ERROR IN DEGREES F = .50
```

Computer Output, Continued

```
N =  58 C =    Q
 115.30   223.80   282.93   322.67   351.66   373.55   390.20   402.67   411.57   417.18
 419.45   417.96   411.64   397.92   370.01   306.09   121.37   255.83   329.81   379.66
 416.03   443.49   464.38   480.06   491.30   498.49   501.66   500.45   493.96   480.47
 457.21   422.01   126.09   289.32   379.02   439.43   483.47   516.70   542.01   561.08
 574.92   584.10   588.86   589.13   584.51   574.43   558.48   537.93   130.98   324.66
 430.98   502.46   554.50   593.72   623.59   646.19   662.80   674.27   681.08   683.48
 681.58   675.51   665.77   653.85   136.17   362.21   486.15   569.30   629.66   675.03
 709.55   735.72   755.17   769.02   778.02   782.73   783.60   781.14   776.11   769.77
 141.72   402.42   545.12   640.55   709.53   761.15   800.29   829.95   852.14   868.26
 879.34   886.19   889.47   889.90   888.30   885.69   147.72   445.84   608.63   717.00
 794.84   852.68   896.26   929.17   953.81   971.91   984.75   993.32   998.48  1001.02
1001.77  1001.61   154.28   493.28   677.75   799.71   886.51   950.35   997.99  1033.68
1060.31  1079.91  1094.02  1103.78  1110.18  1114.05  1116.23  1117.53   161.57   545.98
 754.05   890.20   985.81  1055.12  1106.12  1143.88  1171.80  1192.28  1207.03  1217.37
1224.32  1228.78  1231.56  1233.45   169.88   605.96   839.96   990.68  1094.46  1168.18
1221.43  1260.21  1288.50  1309.04  1323.73  1333.97  1340.80  1345.10  1347.69  1349.37
 179.71   676.70   939.42  1104.41  1214.79  1291.04  1344.77  1383.10  1410.58  1430.24
1444.09  1453.54  1459.59  1463.05  1464.67  1465.29   192.01   764.72  1058.97  1236.20
1349.81  1425.39  1477.00  1512.90  1538.12  1555.83  1568.05  1576.08  1580.78  1582.76
1582.62  1581.21   208.98   883.56  1209.91  1392.94  1503.12  1572.83  1618.67  1649.66
1670.95  1685.61  1695.46  1701.59  1704.56  1704.63  1701.92  1697.13   239.07  1064.67
1411.59  1583.52  1678.04  1734.23  1769.64  1792.89  1808.53  1819.10  1826.00  1829.98
1831.23  1829.42  1823.59  1813.05   356.41  1389.48  1693.95  1816.03  1875.50  1908.51
1928.50  1941.31  1949.79  1955.44  1959.04  1960.94  1961.06  1958.53  1950.54  1928.98
1612.75  2060.73  2081.18  2086.95  2089.70  2091.22  2092.14  2092.73  2093.12  2093.38
2093.54  2093.63  2093.63  2093.49  2092.07  2044.90
```

```
TEMPERATURE DISTRIBUTION AROUND A COPPER CONVERTER TUYERE

DATA

DISTANCE FROM TUYERE IN SPACES =  16
REFRACTORY THICKNESS IN SPACES =  16
MAXIMUM NUMBER OF ITERATIONS = 100
SCALE IN SPACES PER FOOT =12.000
TUYERE RADIUS IN FEET =  .0625
MELT TEMPERATURE IN DEGREES FAHRENHEIT = 2100
BLAST TEMPERATURE IN DEGREES FAHRENHEIT =  100
AIR TEMPERATURE IN DEGREES FAHRENHEIT =  100
HBLAST, BTU PER HR-SQ FT-F = 10.0
HMELT, BTU PER HR-SQ FT-F =500.0
HAIR, BTU PER HR-SQ FT-F =  6.0
THERMAL CONDUCTIVITY OF REFRACTORY, BTU-FT PER HR-SQ FT-F =  2.0
ERROR IN DEGREES F = .50

N =  93 C =    Q
 187.54   324.10   374.13   401.84   420.29   433.60   443.47   450.79   456.00   459.35
 460.86   460.35   457.29   450.38   436.11   403.13   307.34   397.22   447.28   479.39
 501.81   518.22   530.49   539.60   546.14   550.38   552.42   552.11   549.02   542.28
 530.50   512.60   377.84   470.96   524.26   560.18   586.05   605.31   619.83   630.71
 638.60   643.90   646.79   647.26   645.17   640.23   632.30   622.07   436.75   543.59
 603.32   643.72   673.08   695.09   711.78   724.37   733.64   740.09   744.00   745.56
 744.86   742.00   737.29   731.54   493.56   616.72   684.48   730.00   763.02   787.77
 806.57   820.81   831.40   838.96   843.93   846.63   847.30   846.26   843.93   841.02
 551.17   691.70   768.31   819.36   856.15   883.61   904.40   920.15   931.94   940.51
 946.43   950.10   951.91   952.26   951.59   950.49   610.87   769.59   855.52   912.29
 952.86   982.90  1005.50  1022.56  1035.33  1044.70  1051.33  1055.73  1058.35  1059.61
1059.98  1059.96   673.57   851.36   946.94  1009.47  1053.65  1086.01  1110.12  1128.17
1141.63  1151.51  1158.56  1163.35  1166.38  1168.10  1168.96  1169.43   740.27   938.17
1043.61  1111.71  1159.13  1193.36  1218.52  1237.14  1250.90  1260.93  1268.05  1272.88
1275.93  1277.64  1278.48  1278.90   812.36  1031.62  1146.95  1220.11  1270.06  1305.43
1330.99  1349.62  1363.19  1372.96  1379.79  1384.29  1386.96  1388.22  1388.53  1388.37
 892.07  1134.17  1258.96  1336.09  1387.34  1422.76  1447.80  1465.71  1478.55  1487.61
1493.77  1497.60  1499.53  1499.92  1499.17  1497.84   983.39  1249.85  1382.59  1461.46
1511.99  1545.82  1569.13  1585.45  1596.91  1604.82  1609.98  1612.88  1613.80  1612.94
1610.57  1607.31  1094.55  1385.71  1522.12  1598.45  1644.96  1674.92  1694.97  1708.69
1718.12  1724.46  1728.39  1730.23  1730.05  1727.73  1723.15  1716.79  1245.46  1554.54
1683.46  1749.25  1786.82  1809.96  1824.97  1835.02  1841.80  1846.25  1848.83  1849.70
1848.68  1845.13  1837.94  1826.26  1494.42  1778.63  1872.76  1914.73  1936.93  1950.02
1958.30  1963.74  1967.36  1969.68  1970.95  1971.19  1970.09  1966.63  1957.91  1935.73
2046.59  2084.80  2089.56  2091.50  2092.53  2093.13  2093.51  2093.76  2093.92  2094.03
2094.09  2094.10  2094.05  2093.86  2092.41  2045.20

**** ALL INPUT DATA HAVE BEEN PROCESSED.
     AT LOC 24032
```

Discussion of Results

The purpose of making the temperature distribution calculation is to determine the corner temperature at the tuyere mouth. This temperature is particularly critical in copper converter operation since a low temperature at this point permits the precipitation of magnetite from the slag which blocks the tuyere and requires that the operation be stopped and the tuyere punched out. Tuyere punching is presently one of the limiting steps in copper production rates and adds to the expense and difficulty of the operation. The results of the calculation show that a more highly insulating refractory at the tuyere wall, which in effect decreases the rate of heat transfer to the incoming air, would increase the theoretical temperature at the tuyere mouth and prevent the precipitation of magnetite from the slag, thus eliminating the necessity of punching the tuyeres.

The accuracy of the result which is obtained depends upon the number of grid points selected. The solution of Krivsky and Schuhmann was carried out by hand calculation and involved first selecting a five inch grid spacing (4×4 matrix), utilizing this calculated temperature distribution to estimate a temperature distribution for making the temperature calculation at the tuyere mouth based on a finer grid spacing in the lower right hand corner.

The calculated result is markedly influenced by the grid spacing as shown by the data in Table I. The calculations carried out for presentation of the example problem were not extended to extremely fine grid sizes because of the time requirement on the computer. One of the major factors in the time requirement, in addition to the number of matrix points, is the accuracy of the initial temperature distribution. In the present problem a linear distribution was assumed between the melt and the outside or ambient air temperature which would be approximate in the case of a perfectly insulated tuyere, but is far from precise in the case considered in the example problem.

TABLE I

Computed Corner Temperatures for Various Grid Spacings
(Allowable Temperature Change at Grid Point, 0.5°F)

Tuyere Heat Transfer Coefficient BTU/hr-ft^2-°F	Matrix Size	Grid Spacing Inches	Iterations	Corner Temperature °F
10	4x4	5	12	2075
10	6x6	3	23	2067
10	11x11	1.5	58	2054
10	16x16	1	93	2047
200	4x4	5	8	1829
200	6x6	3	17	1753
200	11x11	1.5	40	1659
200	16x16	1	58	1613

The program compiled in 0.46 minutes and 7.01 minutes of execution time on the IBM 709 were required to generate Table I.

Critique

The problem has not been used in the classroom. It appears, however, to be an excellent application of the computer in the teaching of extractive metallurgy since it is a problem which is well adapted to the computer. As discussed by the authors of the reference, the calculation is an extremely laborious and time consuming process when carried out by hand. The presentation of the problem and its importance in copper processing as well as the details of the solution are more than adequately discussed in the reference paper which would serve as an excellent guide to the student in preparing a computer solution to the problem.

Example Problem No. 96

DIGITAL COMPUTER ANALYSIS OF GALVANIC CELL DATA

by

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The University of Michigan

Course: Thermodynamics Credit Hours: 4 Level: Junior

This course presents the basic thermodynamic principles as applied to engineering processes and includes a laboratory which stresses the experimental techniques for measuring thermodynamic parameters.

Statement of Problem

The problem selected for computer analysis is the processing of data taken in the laboratory on high temperature galvanic cells. The purpose of the experiment is to measure the thermodynamic properties of metal alloys. The experiment consists of equilibrating electrodes of binary metallic systems immersed in a molten salt bridge and determining the electromotive force between the electrodes and a pure metal standard electrode. These cell potentials are measured at several temperatures and for several compositions across the binary alloy system. The data is utilized to determine the activity and activity coefficient of one alloying element at various temperatures and composition levels. The problem is amenable to measurements made in chemical systems, and could be modified for use with activity measurements determined by other experimental techniques. This program could also be modified to include calculations of the slope of the EMF-temperature curve by a least-squares fit through the data. Utilizing these slopes, the heat of solution and entropy of solution could be computed.

Write and test a MAD program which will permit the calculation of activities and activity coefficients from a series of electromotive force measurements on several binary alloys at discrete temperatures.

Experiment: The data as measured in the laboratory are presented in the form of weights of the two elements in each electrode and a series of cell potentials measured at several temperatures.

Test Data: Weighings

	gms Cadmium	gms Tin
Cell (1)	1.1785	11.4400
Cell (2)	2.2578	10.8039
Cell (3)	2.4115	9.9616
Cell (4)	2.6463	9.8081
Cell (5)	4.1233	7.7739
Cell (6)	5.1567	4.6476
Cell (7)	9.3444	1.3422

Galvanic Cell Data

EMF Recordings

Temperature, °C	Cell (1)	Cell (2)	Cell (3)	Cell (4)	Cell (5)	Cell (6)	Cell (7)
445	57.33	39.76	36.76	34.62	23.82	15.21	5.13
446	57.29	39.83	36.72	34.56	23.73	14.97	5.18
444	57.35	39.76	36.76	34.56	23.87	15.07	5.16
492	62.18	44.24	40.93	38.58	26.14	16.83	5.67
492	62.20	44.26	41.03	38.64	26.09	16.87	5.71
492	62.17	44.18	40.94	38.58	26.11	16.85	5.71
525	64.60	46.59	43.16	40.70	27.28	17.88	6.04
525	64.59	46.63	43.16	40.75	27.26	17.91	6.04
525	64.59	46.71	43.34	40.84	27.26	17.91	6.08
553	70.19	49.14	45.58	42.98	29.00	19.01	6.41
553	69.79	49.12	45.57	42.99	29.33	19.03	6.37
553	69.91	49.29	45.72	43.13	29.05	19.08	6.53

At. Wt. Cadmium 112.41
Tin 118.70

Solution

In order to assure equilibrium conditions during the experiment, the cell potentials are measured at periodic intervals and at as constant a temperature as possible. The data are then in the form of several temperatures and the EMF associated with each temperature for a given series of alloy compositions. The program will consist of the following steps:

1. Utilizing the weights of alloying elements and the molecular weights of each element, the weight of each element, the weight percentage and the mole fraction of transferred component will be computed for each cell.
2. The average temperature and EMF associated with each set of cell measurements will be computed.
3. The activity for each cell at each temperature will be calculated.
4. The activity coefficient for each cell at each temperature will be computed.

The program as outlined above consists of a series of loops which involve calculations of averages and evaluation of thermodynamic formuli. The relationships which are pertinent to the solution of this problem are summarized as:

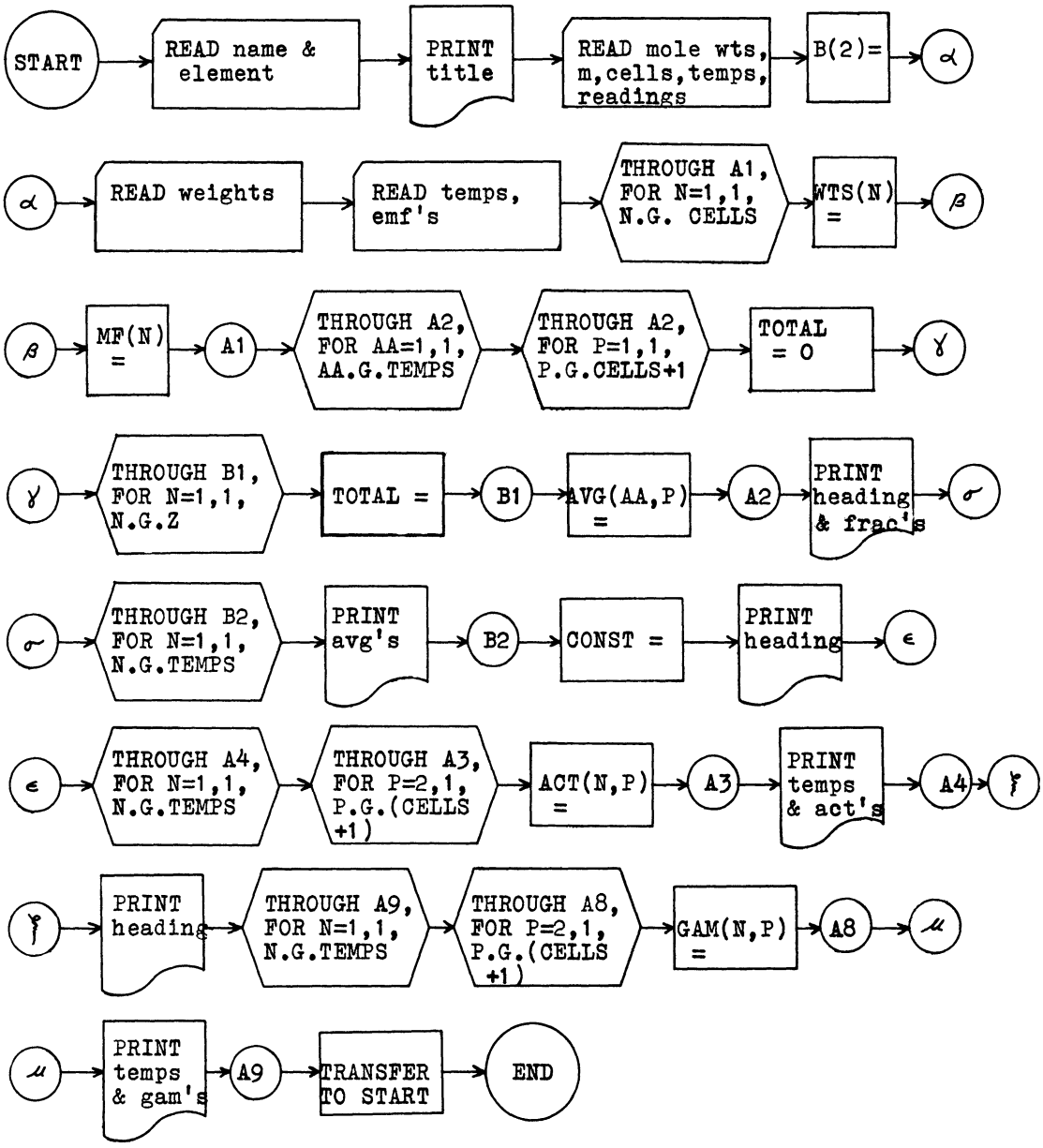
1. The thermodynamic activity of an alloying element in solution, given by the equation:

$$\ln a = \frac{-\eta FE}{RT}$$

2. The activity coefficient of an element in solution, given by the equation:

$$\gamma_i = \frac{a_i}{N_i}$$

Flow Diagram



MAD Program

```
          DIMENSION  WT(100,A),X(900,B),MF(50),WTS(50),AVG(400,B),
         1 ACT(400,B), GAM(400,B)
          VECTOR VALUES A= 2,1,2
          VECTOR VALUES B= 2,1,4
          INTEGER TEMPS,CELLS, M, N, P, AA ,Z
START     READ FORMAT NAME,NA1,NA2,NA3,NA4,NA5, NB1
          PRINT FORMAT TITLE, NA1, NA2, NA3, NA4, NA5
          READ FORMAT DATA,MOLEB,MOLEC,M,CELLS,TEMPS,Z
          B(2)= CELLS+1
          READ FORMAT WEIGHT, WT(1,1)...WT(CELLS,2)
          READ FORMAT NUMBER, X(1,1)...X(Z*TEMPS,CELLS+1)
          THROUGH A1,FOR N=1,1,N.G.CELLS
          WTS(N)= 1./(1.+ WT(N,2) /WT(N,1))
A1        MF(N)=1./(1.+(WT(N,2)/MOLEC)*MOLEB/WT(N,1))
          THROUGH A2, FOR AA=1,1, AA.G.TEMPS
          THROUGH A2, FORP=1,1, P.G.CELLS+1
          TOTAL = 0.0
          THROUGH B1, FOR N=1,1, N.G. Z
B1        TOTAL = X(N+Z*(AA-1),P )  + TOTAL
A2        AVG(AA,P) = TOTAL/Z
          PRINT FORMAT SUB0
          PRINT FORMAT HEAD1,NB1, MF(1)...MF(CELLS)
          PRINT FORMAT HEAD2, WTS(1)...WTS(CELLS)
          PRINT FORMAT TEMPER
          THROUGH B2, FOR N=1,1,N.G.TEMPS
B2        PRINT FORMAT THREE, AVG(N,1)...AVG(N,CELLS+1)
          CONST=-23.066*M/1.987
          PRINT FORMAT SUB1
          PRINT FORMAT HEAD1,NB1, MF(1)...MF(CELLS)
          PRINT FORMAT HEAD2, WTS(1)...WTS(CELLS)
          PRINT FORMAT TEMPER
          THROUGH A4, FOR N=1,1,N.G.TEMPS
          THROUGH A3,FOR P=2,1,P.G.(CELLS+1)
A3        ACT(N,P)= EXP.(CONST*AVG(N,P)/(AVG(N,1)+273.16))
A4        PRINT FORMAT TWO, AVG(N,1), ACT(N,2)...ACT(N,P-1)
          PRINT FORMAT SUB4
          PRINT FORMAT HEAD1,NB1, MF(1)...MF(CELLS)
          PRINT FORMAT HEAD2, WTS(1)...WTS(CELLS)
          PRINT FORMAT TEMPER
          THROUGH A9,FOR N=1,1,N.G.TEMPS
          THROUGH A8,FOR P=2,1,P.G.(CELLS+1)
A8        GAM(N,P) = ACT(N,P)/ MF(P-1)
A9        PRINT FORMAT TWO, AVG(N,1), GAM(N,2)...GAM(N,P-1)
          TRANSFER TO START
          VECTOR VALUES NAME=$ 5C6, S8, C2     *$
          VECTOR VALUES TITLE=$ 1H1, S40, 32H ELECTROLYTIC CELL MEASURE
         1MENTS       //  S56, 4H OF      // S47, 5C6   ////// *$
          VECTOR VALUES DATA=$ 2F10.5, 4I10      *$
          VECTOR VALUES WEIGHT=$ (6F10.5)  *$
          VECTOR VALUES NUMBER=$(7F10.5)  *$
          VECTOR VALUES SUB0=$ 1H0,S45,31H AVERAGE OF EXPERIMENTAL DATA
         I     ///  *$
          VECTOR VALUES SUB1=$ 1H1, S52, 10H ACTIVITY   ///*$
          VECTOR VALUES SUB4=$ 1H1, S45, 22H ACTIVITY COEFFICIENT ///*$
          VECTOR VALUES HEAD1=$ 10H ELEMENT    , C2, / 16H MOLE FRACTION
         I      S3,  9F11.6      *$
          VECTOR VALUES HEAD2=$  18H WEIGHT FRACTION      , S1, 9F11.6*$
          VECTOR VALUES TEMPER=$  15H TEMPERATURE C  /    *$
          VECTOR VALUES  ANS=$ /  S19,  9F11.4     *$
          VECTOR VALUES TWO=$ / S3, F9.2, S7, 9E11.5    *$
          VECTOR VALUES THREE=$  / S3,  F9.2, S7, 9F11.3     *$
          END OF PROGRAM
```

Data

The format used for putting the data into the computer program was as follows:

First Data Card

Columns 1-30 contain the title of the experiment.

Columns 39-40 contain the symbol of the element under investigation.

Second Data Card

Columns 1-10 contain the atomic weight of the element under investigation.

Columns 11-20 contain the atomic weight of the alloying element.

Columns 21-30 contain the number of electrons involved in the transfer.

Columns 31-40 contain the number of different electrodes investigated.

Columns 41-50 contain the number of different temperatures investigated.

Columns 51-60 contain the number of readings taken per temperature setting.

Weight Information Cards

Columns 1-60 are used on each card and are divided into six groups of ten. Three complete electrode weights can be placed on one card. The weight of the major element and then the alloying element are listed for each electrode.

Temperature and EMF Cards

Columns 1-70 are used on each card and are divided into seven groups of ten. The temperature and then the EMF readings are listed across the card. The list continues until the data is complete.

Below is a sample printout of the Cadmium-Tin data used as the example problem.

```
$DATA
CADMIUM IN CD-SN ALLOYS                                    CD
112.41    118.7                2          7          4          3
1.1785    11.44     2.2578     10.8039    2.4115     9.9616
2.6463    9.8081    4.1233     7.7739     5.1567     4.6476
9.3444    1.3422
445.      57.33     39.76      36.76      34.62      23.82      15.21
5.13      445.      57.29      39.83      36.72      34.56      23.73
14.97     5.18      445.       57.35      39.76      36.76      34.56
23.87     15.07     5.16       492.       62.18      44.24      40.93
38.58     26.14     16.83      5.67       492.       62.20      44.26
41.03     38.64     26.09      16.87      5.71       492.       62.17
44.18     40.94     38.58      26.11      16.85      5.71       525.
64.60     46.59     43.16      40.70      27.28      17.88      6.04
525.      64.59     46.63      43.22      40.75      27.26      17.91
6.04      525.      64.59      46.71      43.71      40.84      27.26
17.91     6.08      553.       70.19      49.14      45.58      42.98
29.00     19.01     6.14       553.       69.79      49.12      45.57
42.99     42.33     19.03      6.37       553.       69.91      49.29
45.72     43.13     29.13      19.08      6.53
```

Computer Output

ELECTROLYTIC CELL MEASUREMENTS

OF

CADMIUM IN CD-SN ALLOYS

AVERAGE OF EXPERIMENTAL DATA

ELEMENT CD							
MOLE FRACTION	.098108	.180780	.203584	.221732	.359008	.539515	.880262
WEIGHT FRACTION	.093395	.172857	.194899	.212479	.346577	.525963	.874403
TEMPERATURE C							
445.00	57.323	39.783	36.747	34.580	23.807	15.083	5.157
492.00	62.183	44.227	40.967	38.600	26.113	16.850	5.697
525.00	64.593	46.643	43.363	40.763	27.267	17.900	6.053
553.00	69.963	49.183	45.623	43.033	33.487	19.040	6.347

ACTIVITY

ELEMENT CD							
MOLE FRACTION	.098108	.180780	.203584	.221732	.359008	.539515	.880262
WEIGHT FRACTION	.093395	.172857	.194899	.212479	.346577	.525963	.874403
TEMPERATURE C							
445.00	.15674E 00	.27634E 00	.30484E 00	.32696E 00	.46318E 00	.61409E 00	.84645E 00
492.00	.15156E 00	.26134E 00	.28851E 00	.30999E 00	.45278E 00	.59973E 00	.84126E 00
525.00	.15276E 00	.25749E 00	.28327E 00	.30552E 00	.45242E 00	.59412E 00	.83855E 00
553.00	.14000E 00	.25104E 00	.27745E 00	.29840E 00	.39022E 00	.58563E 00	.83665E 00

ACTIVITY COEFFICIENT

ELEMENT CD							
MOLE FRACTION	.098108	.180780	.203584	.221732	.359008	.539515	.880262
WEIGHT FRACTION	.093395	.172857	.194899	.212479	.346577	.525963	.874403
TEMPERATURE C							
445.00	.15976E 01	.15286E 01	.14974E 01	.14746E 01	.12902E 01	.11382E 01	.96159E 00
492.00	.15448E 01	.14456E 01	.14171E 01	.13980E 01	.12612E 01	.11116E 01	.95570E 00
525.00	.15571E 01	.14243E 01	.13914E 01	.13779E 01	.12602E 01	.11012E 01	.95262E 00
553.00	.14270E 01	.13886E 01	.13628E 01	.13458E 01	.10869E 01	.10855E 01	.95045E 00

**** ALL INPUT DATA HAVE BEEN PROCESSED.

Discussion of Results

The computer program prints out three tables which list the averages of the data, the activities, and the activity coefficients for the various values of temperature and composition investigated.

The MAD program compiled in 0.52 minutes and performed all the required operations for the Cadmium-Tin example in 0.34 minutes of execution time.

Concerning the results, it is important to realize that the number of significant figures presented by the computer are not necessarily correct, but instead depend on the number of significant figures in the original data.

Critique

This particular problem is especially well suited to a laboratory course in which a series of data are taken and require considerable time for analysis. This particular problem has not been used in instruction of the course in thermodynamics, but would be especially well suited to the laboratory supplement to the course.

One important use of the computer in laboratories and engineering sections of industrial organizations is for routine data analysis. In many cases, small computers are especially well-suited for this application. To emphasize this aspect of computer use would be of particular benefit to the engineering student. The program for analyzing electromotive force measurements has been used in research work at The University of Michigan, and although it has not been prepared for the small computer, the program would be especially well suited to it.

The program contains several computing steps involving data averaging, and formula evaluation. The problem, thus, appears to be well suited for the purpose of illustrating data analysis using the digital computer.

VII. REFERENCES

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