NBS SPECIAL PUBLICATION 486

U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards

User Evaluation of "Phase Diagrams for Ceramists" and Implications for Related Data and Research Programs

NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards[1] was established by an act of Congress March 3, 1901. The Bureau's overall goal is to strengthen and advance the Nation's science and technology and facilitate their effective application for public benefit. To this end, the Bureau conducts research and provides: (1) a basis for the Nation's physical measurement system, (2) scientific and technological services for industry and government, (3) a technical basis for equity in trade, and (4) technical services to promote public safety. The Bureau consists of the Institute for Basic Standards, the Institute for Materials Research, the Institute for Applied Technology, the Institute for Computer Sciences and Technology, the Office for Information Programs, and the Office of Experimental Technology Incentives Program.

THE INSTITUTE FOR BASIC STANDARDS provides the central basis within the United States of a complete and consistent system of physical measurement; coordinates that system with measurement systems of other nations; and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. The Institute consists of the Office of Measurement Services, and the following center and divisions:

Applied Mathematics — Electricity — Mechanics — Heat — Optical Physics — Center for Radiation Research — Laboratory Astrophysics[2] — Cryogenics[2] — Electromagnetics[2] — Time and Frequency[2].

THE INSTITUTE FOR MATERIALS RESEARCH conducts materials research leading to improved methods of measurement, standards, and data on the properties of well-characterized materials needed by industry, commerce, educational institutions, and Government; provides advisory and research services to other Government agencies; and develops, produces, and distributes standard reference materials. The Institute consists of the Office of Standard Reference Materials, the Office of Air and Water Measurement, and the following divisions:

Analytical Chemistry — Polymers — Metallurgy — Inorganic Materials — Reactor Radiation — Physical Chemistry.

THE INSTITUTE FOR APPLIED TECHNOLOGY provides technical services developing and promoting the use of available technology; cooperates with public and private organizations in developing technological standards, codes, and test methods; and provides technical advice services, and information to Government agencies and the public. The Institute consists of the following divisions and centers:

Standards Application and Analysis — Electronic Technology — Center for Consumer Product Technology: Product Systems Analysis; Product Engineering — Center for Building Technology: Structures, Materials, and Safety; Building Environment; Technical Evaluation and Application — Center for Fire Research: Fire Science; Fire Safety Engineering.

THE INSTITUTE FOR COMPUTER SCIENCES AND TECHNOLOGY conducts research and provides technical services designed to aid Government agencies in improving cost effectiveness in the conduct of their programs through the selection, acquisition, and effective utilization of automatic data processing equipment; and serves as the principal focus wthin the executive branch for the development of Federal standards for automatic data processing equipment, techniques, and computer languages. The Institute consist of the following divisions:

Computer Services — Systems and Software — Computer Systems Engineering — Information Technology.

THE OFFICE OF EXPERIMENTAL TECHNOLOGY INCENTIVES PROGRAM seeks to affect public policy and process to facilitate technological change in the private sector by examining and experimenting with Government policies and practices in order to identify and remove Government-related barriers and to correct inherent market imperfections that impede the innovation process.

THE OFFICE FOR INFORMATION PROGRAMS promotes optimum dissemination and accessibility of scientific information generated within NBS; promotes the development of the National Standard Reference Data System and a system of information analysis centers dealing with the broader aspects of the National Measurement System; provides appropriate services to ensure that the NBS staff has optimum accessibility to the scientific information of the world. The Office consists of the following organizational units:

Office of Standard Reference Data — Office of Information Activities — Office of Technical Publications — Library — Office of International Standards — Office of International Relations.

---

[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D.C. 20234.

[2] Located at Boulder, Colorado 80302.

User Evaluation of "Phase Diagrams for Ceramists" and Implications for Related Data and Research Programs

t Special Publication 486

R.S. Roth, L.P. Cook, T. Negas,
G.W. Cleek, and J.B. Wachtman, Jr.

Institute for Materials Research
National Bureau of Standards
Washington, D.C. 20234

U.S. DEPARTMENT OF COMMERCE, Juanita M. Kreps, Secretary

Dr. Sidney Harman, Under Secretary

Jordan J. Baruch, Assistant Secretary for Science and Technology

NATIONAL BUREAU OF STANDARDS, Ernest Ambler, Acting Director

Issued August 1977

Library of Congress Cataloging in Publication Data

Main entry under title:

User evaluation of "Phase diagrams for ceramists" and implications for related data and research programs.

(NBS special publication ; 486)

Based on responses to a questionnaire distributed by the American Ceramic Society.

Supt. of Docs. no. C13.10:486

1. Phase diagrams. I. Roth, Robert Sidney. II. American Ceramic Society. III. Levin, Ernest M. Phase diagrams for ceramists. IV. Series: United States. National Bureau of Standards. Special publication ; 486.

QC100.U57 no. 486 [QD503] 602'.1s [666] 77-10496

National Bureau of Standards Special Publication 486

Nat. Bur. Stand. (U.S.), Spec. Publ. 486, 70 pages (Aug. 1977)

CODEN: XNBSAV

U.S. GOVERNMENT PRINTING OFFICE

WASHINGTON: 1977

For sale by the Superintendent of Documents, U.S. Government Printing Office

Washington, D.C. 20402 - Price $2.10

Stock No. 003-003-01827-9

TABLE OF CONTENTS

USER EVALUATION OF "PHASE DIAGRAMS FOR CERAMISTS" AND IMPLICATIONS FOR RELATED DATA AND RESEARCH PROGRAMS

R.S. Roth, L.P. Cook, T. Negas, G.W. Cleek, and J.B. Wachtman, Jr.

Institute for Materials Research
National Bureau of Standards
Washington, D.C. 20234

Abstract

A survey was made of the needs of the users of "Phase Diagrams for Ceramists," a continuing special publication series published by the American Ceramic Society under the general editorship of the National Bureau of Standards. The results overwhelmingly support continuation of the series, but point to needs for expanded coverage, fuller commentaries, and reduced publication time. The results also identify needs for greater effort on specific types of experimental and theoretical phase equilibria studies including the effects of variable oxygen pressure and complex metal-ceramic systems.

Key Words: American Ceramic Society; ceramics; phase diagrams, "Phase Diagrams for Ceramists"; phase equilibria; user evaluation

1.0 Introduction

Phase diagrams play an important role in the development of ceramic materials. Phase equilibria data are essential in meeting the expanding needs for refractories, electronic components, non-crystalline solids, and various other applications of interest to ceramic scientists and engineers. The chemical information generally summarized as a phase equilibrium diagram is extremely useful in many industrial processes. However, the necessary research involved in obtaining such information is often very costly. The average binary phase diagram can be estimated to take about one man year and a ternary diagram may take five times that effort. To avoid duplication, it is advantageous to have all existing diagrams compiled and distributed for easy access.

As described below, the American Ceramic Society long ago recognized the importance of phase diagrams to the field of ceramic materials and the importance of having this type of information available in evaluated and summarized form. Beginning in 1933, the Society has worked continuously with the National Bureau of Standards to provide a sequence of reports under the title "Phase Diagrams for Ceramists" giving evaluated data from the literature on selected ceramic systems. The Bureau has supplemented these data with measurements in its own laboratories on a limited number of systems chosen because the data were needed for specific reasons but were not available or were of doubtful accuracy. Other laboratories such as the Geophysical Laboratory of the Carnegie Institute and the Pennsylvania State University have supported "Phase Diagrams for Ceramists" through evaluations by their staffs and/or through experimental work. The overall responsibility and general editorship have, however, always been assumed by the National Bureau of Standards.

Several valuable contributions to compilation, evaluation, and publication of phase diagrams of ceramic systems have been made by other groups and published independently from time-to-time as described below. These have generally been one-time-only activities with a limited, specialized scope. "Phase Diagrams for Ceramists" is the only continuing program of general scope in the Western World. With the recent addition of an International Board of Contributing Editors, it appears very likely to be even more central and unique in the future.

Planning and management of "Phase Diagrams for Ceramists" has been done primarily on the basis of informal assessment of user needs through personal contacts by the editors. A more organized and widespread assessment of user needs was, however, thought to be desirable because of several factors. The joint work of the various contributors to "Phase Diagrams for Ceramists" has increased greatly in scope and volume. Not only has the volume of ceramics in production increased but so has the number of types of ceramics and the application in industries outside those traditionally regarded as "ceramic" industries (including glass). Increasing sophistication in processing and increasing demands for durability in service place more stringent demands on phase diagram data to support processing and maintenance in service. Also, requests by individual users for more extensive evaluation and information has increased the work required for each diagram.

To systematically assess user needs a questionnaire was devised jointly by the American Ceramic Society and the National Bureau of Standards. The primary purpose was to determine how well "Phase Diagrams for Ceramists" is meeting user needs and what changes and expansions of scope, if any, are needed. A secondary purpose was to assess the users' feelings for what areas of phase equilibria determination (as opposed to compilation and evaluation) are most needed.

2.0 Brief History of Phase Diagrams for Ceramists and Related Activities

2.1 General Phase Diagrams

The major references in English for phase equilibria data are:

- E. M. Levin, et al., "Phase Diagrams for Ceramists" (3 volumes)

- G. J. Janz, et al., "Molten Salts" (4 volumes)

There is some duplication of compilation activity in the ceramic sciences but this is largely an international problem. The principal compilations in addition to "Phase Diagrams for Ceramists" are Russian. Such duplication is not necessarily wasteful, since any publication would have to be made available in both languages. Also, the two groups of publications, which are partly independent, can be cross-checked for inclusion of references otherwise missed.

The U.S.S.R. publications include:

- N. A. Toropov, et al., "Handbook of Phase Diagrams of Silicate Systems" (English translations available from NTIS)

- V. P. Barzanovskii, et al., "Phase Diagrams of the Silicate Systems:, 2 volumes (in Russian)

- D. L. Ageeva, "Phase Diagrams of Non-Metallic Systems", 10 volumes (in Russian)

- F. V. Chukov, "Minerals: Phase Diagrams of Importance to Mineral Formation" (2 volumes - in Russian)

In Japan compilation activities have, so far, been confined mainly to refractories. These include:

- S. Somiya, "Zirconia Bearing Refractories" (in Japanese)

2.2 Compilation Activities - Metal Oxygen Systems

The link between metallurgy and ceramics is found in the equilibria data for the binary metal-oxygen systems. Special compilation activities in the United States for these systems began in 1961 with a group of reports by J. H. Westbrook, R. E. Carter and R. C. DeVries:

I. Rare Earth Metal - Oxygen Systems
II. Alkaline Earth - Oxygen Systems
III. Precious Metal - Oxygen Systems

Another compilation has been published in India by B. K. Rajput, A. M. George and M. D. Karkhanavala and pertinent portions will be included in the next supplement of "Phase Diagrams for Ceramists". The proceedings of the Workshop on Applications of Phase Diagrams in Metallurgy and Ceramics, held at NBS January 10-12, 1977, contain a report of a more ambitious compilation attempt by W. B. White for the metal-oxygen systems (paper MPSI-5).

2.3 Phase Diagrams for Ceramists

The history of the compilation of Phase Diagrams for Ceramists dates back to 1933, when 157 diagrams collected by F. P. Hall* and Herbert Insley** were published in the October issue of the Journal of the American Ceramic Society. A supplement was published in the April 1938 issue of the same journal. A complete compilation of the diagrams appeared as Part II of the November 1947 Journal and contained 485 diagrams. In December 1949, H. F. McMurdie** and F. P. Hall were authors of a supplement to the 1947 edition. In January 1956, the American Ceramic Society published a separate volume of phase diagrams edited by E. M. Levin**, H. F. McMurdie and F. P. Hall. Part II of this volume appeared in 1959 authored by E. M. Levin and H. F. McMurdie. In 1964, a new complete compilation containing 2066 diagrams was published with E. M. Levin, H. F. McMurdie, and C. R. Robbins** as authors. A supplement to the 1964 volume appeared in 1969 and contained another 2183 diagrams.

* Pass and Seymour, Inc., Syracuse, N.Y.
** National Bureau of Standards

A third volume or second supplement, published in 1975 (850 diagrams), includes a discussion of the methods, data and interpretations made in the construction of each diagram. Since the death of E. M. Levin in 1974, this effort is being continued by a team of scientists actively engaged in phase equilibria studies in research centers in this country and abroad. This group is led by researchers at NBS who are assuming the responsibility for collecting data from the literature, distributing it among the group for evaluation, coordinating preparation of the publication, and preparing evaluations of systems in their own areas of expertise. A third supplement is planned for publication in 1978.

This latest supplement will include critical commentaries discussing preparation of starting materials, experimental methods, characterization of products, accuracy and precision of data and of diagrams. Scientists at NBS (L. Cook, R. Roth and T. Negas) with the help of the American Ceramic Society (G. Cleek) are assuming much of the responsibility for gathering the data from the literature and coordinating the preparation of evaluations and final editing of diagrams. The following experts in various fields are serving as Contributing Editors for the 1978 Supplement:

- J. J. Brown, Jr., Virginia Polytechnic Inst.
  Fluoride containing systems

- L. L. Y. Chang, Miami Univ.
  Tungstates, molybdates, carbonates

- R. C. DeVries, General Electric Co.
  High pressure studies

- F. P. Glasser, Univ. Aberdeen
  Alkali oxide containing systems

- F. A. Hummel, Pennsylvania State Univ.
  Sulfides, phosphates

- A. Muan, Pennsylvania State Univ.
  First row transition metal oxide containing systems

- C. Semler, Ohio State Univ.
  Anhydrous silicate - oxide systems

- C. A. Sorrell, Univ. Missouri-Rolla
  Aqueous salt systems

- K. H. Stern, Naval Research Laboratory
  Binary systems with halides only

- R. E. Thoma, Oak Ridge National Laboratory
  Fused salts

- T. Y. Tien, Univ. of Michigan
  Nitrides, oxynitrides

- D. R. Wilder and M. F. Berard, Iowa State Univ.
  R. E. oxide bearing systems

- H. S. Yoder, Jr., Carnegie Inst. Washington
  Hydrous silicate systems, high pressure silicate studies

Coverage according to chemical system for the various editions is as follows:

	1964	1969	1975	1978
Metal-oxygen systems	146	202	104	∿205
Metal oxide systems	855	408	401	∿655
Systems with oxygen containing radicals	172	228	68	∿120
Systems with halides only	483	718	145	∿365
Systems containing halides with other substances	214	273	72	∿160
Systems containing cyanides, sulfides, etc.	43	82	20	∿140
Systems containing water	151	131	40	∿250

In addition to the compilation "Phase Diagrams for Ceramists", the American Ceramic Society publishes a series of large-scale ternary phase diagrams. There are currently ten diagrams in this series which were originally prepared by E. F. Osborn and A. Muan of the Pennsylvania State Univ. Several new diagrams will be published in this series in the near future and the originals will be reviewed for possible updating. Dr. E. F. Osborn discussed the preparation of these diagrams and the world-wide research effort which made them possible during his Orton Memorial Lecture delivered before the 72nd Annual Meeting of the American Ceramic Society, May 4, 1970, (published in The Bull. Am. Ceram. Soc., 49, 702-706, 1970). In the introduction to this talk, Dr. Osborn says:

> "I want to sketch briefly the history of a development of extreme importance in the emergence of ceramic technology in the United States. ---to reflect on the remarkable development of a science which has become the base of ceramic technology.
>
> "The science to which I refer deals with phase relations in oxide and related systems, ---depicted by the phase diagrams so familiar to ceramic scientists and engineers."

In conclusion, Osborn notes:

> "We need continuing development of theoretical, basic experimental and applied research. We need in addition the means of disseminating the information in an optimum way. ---the assembling and republishing of diagrams to make the accumulating data more readily useful to ceramists was accomplished through the efforts of a government laboratory, the National Bureau of Standards, with publication by the American Ceramic Society."

3.0 Phase Diagrams for Ceramists - Survey of Users

A questionnaire was distributed by the American Ceramic Society in July 1976 to purchasers of the 1975 Supplement of "Phase Diagrams for Ceramists". The total number of questionnaires distributed was 460. The total number returned in the first three months was 186. This is a response of 40%, a remarkably large percent return, illustrating the great interest in the user community in this compilation. Table 1 gives the statistical breakdown of the origin of the returns. It should be noted that 81 or 44% of these are of domestic industrial users. Nine questionnaires were returned after the October 1 deadline, only one of which was identified as a domestic industrial user and are not included in this analysis. The large response allows a determination of user needs in phase equilibria with a reasonably high statistical probability of success. A copy of the questionnaire is given in Appendix 1 with a statistical summary of the answers shown for each question.

Table 1. PHASE DIAGRAMS FOR CERAMISTS PRELIMINARY RESULTS OF SURVEY OF USERS

Total Number Distributed - 460

Total Number Returned in First Three Months - 186

Response - 40%

- Unidentified - 25 (13%)
- Foreign - 37 (20%)
- Domestic
  1. Government and National Laboratories - 5 (3%)
  2. University and Non-Profit Laboratories - 38 (20%)
  3. Industrial - 81 (44%)

In this questionnaire, twenty-one questions were asked covering the four major categories:

I. Description of Respondent (1-7)
II. Uses of Phase Equilibria Data and Principles (8-10)
III. Evaluation of Phase Diagrams for Ceramists as a Publication of the American Ceramic Society (11-18)
IV. Important Needs for Experimental and/or Theoretical Work (not now being done) (19-21)

3.1 Description of Respondents (I)*

3.1.1 Personal Data

The first seven questions requested personal data and nature of employment. Under Type of Training 127 individuals (68%) identified themselves as scientists while 71 (38%) refer to themselves as engineers, with only four (or 2%) belonging to the "other" category. As scientists and engineers add up to more than 100%

* Roman numeral in parenthesis indicates Major Category

obviously some identify themselves with both groups. This breakdown along with the highest degree of the respondent is shown in Table 2. Note that 62% have a Ph.D. or equivalent. Their highest degree was generally in the fields of ceramics, chemistry, materials or geology (Table 3). In Table 4 the present type of work checked by the respondent is summarized by total number and percent. As the respondent was asked to check as many as appropriate, the totals again are greater than 100%. By far the largest group is in research and development although technical management and education activities are well represented. As shown in Table 5, 83% identify themselves as members of the American Ceramic Society and their division affiliations are mostly Basic Science, Refractories, Glass and Electronics.

Table 2. DESCRIPTION OF RESPONDENT (I)

Type of Training (1)

- Scientist - 127 (68%)
- Engineer - 71 (38%)
- Other - 4 (2%)

Highest Degree (2)

- BS or BA - 31 (17%)
- MS or MA - 30 (16%)
- PhD or ScD - 115 (62%)
- OTHER - 10 (5%)

Table 3. SPECIFIC FIELD OF HIGHEST DEGREE (2)

1. Ceramics (Technology, Engineering, Science) - 56 (30%)
2. Chemistry (Physical, Inorganic, Engineering, Industrial, Electrochemistry, etc.) - 40 (22%)
3. Materials Science (Engineering) - 17 (9%)
4. Geology - Mineralogy - 16 (9%)
5. Metallurgy - 12 (6%)
6. Physics - 5
7. Engineering - 4
8. Crystallography - 1
9. Natural Sciences - 1
10. No Identification - 33 (18%)

Table 4. PRESENT TYPE OF WORK (3)

- Research - 143 (77%)
- Development - 85 (46%)
- Production - 18 (10%)
- Technical Management - 40 (22%)
- Education - 46 (25%)
- Other - 9

Table 5. MEMBERSHIP IN THE AMERICAN CERAMIC SOCIETY (4a)

- Yes - 155 (83%)
- No - 28 (15%)

DIVISION AFFILIATION (4b)

1) Basic Science - 56

Cement - 4

Ceramic-Metal Systems - 5

4) Electronics - 21

3) Glass - 23

Materials and Equipment - 4

Nuclear - 5

2) Refractories - 29

Structural Clay Products - 1

White Wares - 1

No Division - 12

3.1.2 Standard Industrial Categories of Employer (5)**

The respondents were requested to check one or more of a group of listed Standard Industrial Categories (SIC) which best describe their employer. Those categories receiving ten or more entries are listed in Table 6. The major industrial categories include stone, clay and glass products, electrical and electronic equipment, chemicals and non-metallic minerals. Thirty-five respondents checked the box marked "Other [please describe in your own words]" and their descriptions for these categories are listed in Table 7. The name and address of the employer was given by 150 respondents and these are shown in Table 8. One hundred and seventy-four listed their own name and address indicating a (conditional) willingness to be contacted for further information.

** Arabic numeral in parenthesis indicates Question Number.

Table 6. STANDARD INDUSTRIAL CATEGORIES OF EMPLOYER (5)

(10 or more checked)

SIC NO.	CATEGORY	NO. OF TIMES CHECKED
32	Stone, Clay and Glass Products	50
82	Educational Services	46
36	Electrical and Electronic Equipment	26
28	Chemicals and Allied Products	20
14	Nonmetallic Minerals, Except Fuels	19
33	Primary Metal Industries	15
34	Fabricated Metal Products	13
38	Instruments and Related Products	10
	Other	35

Table 7. STANDARD INDUSTRIAL CATEGORIES (5)

Other: 35

Industry

1. Foundries
2. Manufacture of granular refractories - dolomite pebble, quick lime
3. Technical ceramics, primarily BeO. Electronic and allied industries major customers
4. Refractories engineering
5. Optical, electronic and solid state materials
6. Photovoltaic materials and devices
7. Ceramics manufacturing - alumina
8. Technical consulting services
9. Aerospace - communications satellite electronics
10. Materials and components for hobby, decorative and electronic industry
11. Speciality metal alloys for industry
12. Lighting products, home entertainment products, communications systems
13. Manufacturers of fiber optics
14. Electrical components
15. Refractories - nonclay

Table 7. STANDARD INDUSTRIAL CATEGORIES (15) - Continued

University and Non-Profit Laboratories

16. Student
17. Univ. basic research, oxides
18. Research on inorganic materials
19. Contract research
20. Research and Development modern H.T. ceramics (borides, carbides, nitrides)
21. National Research Laboratory

Government and National Laboratories

22. Exploration and utilization of space
23. Research (energy, physics, biology, etc.)

Unidentified

24. Engineers to Glass and Steel
25. R&D for ERDA

Foreign

26. Refractories industry - manufacture and usage
27. Reprocessor of nuclear fuels
28. Refractories manufacture
29. Research in Ceramics and Powder Met.
30. Innovation of Minerals Application to new Technology

Table 8. PERSONAL EMPLOYMENT DATA (6)

INDUSTRIAL

AVX Ceramics
Babcock & Wilcox
J. E. Baker Co.
Bell Laboratories (3)
Frank B. Black Res. Center
Bourns, Inc.
Brockway Glass Co. (4)
Champion Spark Plug Co
Columbia Gas System Service Corp.
Combustion Engineering Inc.
Consolidated Ceramics and Metallizing Corp.
Corning Glass Works (3)
Cyprus Research Co.
M. H. Detrick Co.
E. I. duPont de Nemours and Co., Inc.
Englehard Industries
Eric Technological Products Inc.
The Exolon Company
Exxon Research & Eng. Co.
Ferro Corporation
Galileo Electro-Optics Corp.
General Electric (3)
General Refractories Company (2)
General Telephone & Electronics
Globe Union, Inc.
W. R. Grace & Co. (2)
Gulf Chemical & Metallurgical Co.
Kelsey Hayes Co.
Horizons Research Inc.
Howmet Corp.
IBM Research
Ideal Basic Industries Inc.
Inco, Inc.
Inland Steel Co.
Interpace Corp.
J. F. Jelenko and Co.
Jones and Laughlin Steel Corp.
Leeds & Northrup Co.
Lithium Corp. of America
A. D. Little, Inc.
Kerr McGee Corp.
McGraw Edison Co.
Metco Inc.
Mobile Tyco Solar Energy Co.

Table 8. PERSONAL EMPLOYMENT DATA (6) - Continued

INDUSTRIAL (Continued)

National Standard Co.
Ohio Brass Co.
Owens-Corning Fiberglas
Owens Illinois Inc.
PPG Industries
Reading Alloys, Inc.
Reynolds Metals Co.
Rockwell International
St. Joe Minerals Corp.
Sanders Associates Inc.
Semi-Alloys
Sherwood Refractories Inc.
Siemens Corp.
Smith Corona Marchant Corp.
TRW, Inc.
Thermo Materials Corp.
Toth Aluminum Corp.
Union Carbide Corp.
Valley Mineral Products Corp.
Western Gold and Platinum Co.
Williams Gold Refining Co.
Xerox Corp.

UNIVERSITY AND NON-PROFIT LABS.

Arizona State Univ.
Brown Univ.
Bryn Mawr College
Carnegie Institution of Washington
Case Western Reserve Univ.
Colorado School of Mines
Georgia Institute of Technology
Iowa State Univ. (2)
Lawrence Berkeley Lab.
Lehigh Univ (2)
MIT (5)
Northwestern Univ. (3)
Ohio State Univ.
Penn State Univ. (3)
Purdue Univ.
State Univ. of N.Y.
SUNY at Stonybrook (2)
Univ. of California
Univ. of Chicago
Univ. of Michigan
Univ. of Pennsylvania
Univ. of Pittsburgh
Univ. of Utah (2)
Vanderbuilt Univ.
Virginia Polytechnic Institute

Table 8. PERSONAL EMPLOYMENT DATA (6) - Continued

GOVERNMENT AND NATIONAL LABORATORIES

Brookhaven National Labs.
Bureau of Mines, Albany
NASA (2)
Oak Ridge National Lab.

FOREIGN (Europe)

N.V. Bekaert S. A. - Belgium
Aalborg Portland Concrete Research Lab. - Denmark
BNFL - England
British Aluminum Co. - England
British Ceramic Research Assoc. - England
British Steel Corp. - England
Thos. Marshall & Co. (Loxley) Ltd. - England
Steetley Co. Ltd. - England
The University of Leeds - England
St. Gobain Industries - France
Ugine Carbone S.A. - France
University of Orleans - France
Friedrich Schejbol - Germany
Max Planck Institut fur Metallforschung - Germany
University of Saarbrucken - Germany
Universita-Dibari - Italy
SANAC Genova - Italy
N. V. ENCI - The Netherlands
N. V. Philips Gloeilampenfabrieken - The Netherlands
Swedish Institute for Silicate Research - Sweden
Battelle Geneva Research Center - Switzerland
Universitat Bern - Switzerland

FOREIGN (Others)

Glass Containers Ltd. - Australia
Industria Brasileira Deartigos Refratarios S. A. - Brazil
C. T. de Freitas - Brazil
Atlantic Research Lab. - Canada
Domglas Ltd. - Canada
Saskatchewan Research Council - Canada
Muki-Zaishits Kenkyusho - Japan
Science College of Okayam - Japan
Solar Research Lab - Japan
Takhiyuki Sata Res. Lab. - Japan
Tokyo Institute of Technology - Japan
University of Tokyo - Japan
National Institute for Metallurgy - South Africa

3.2 Uses of Phase Equilibria Data and Principles (II)

3.2.1 Applications (8-9)

Question eight asked for areas of application of phase equilibria in the respondent's organization (check as many as possible). Fifteen categories were listed while the sixteenth, entitled "Other", requested specifics. Table 9 lists these categories rearranged according to decreasing number of responses. Nineteen respondents checked the box labelled "Other [please specify]" and their designated areas of application of phase equilibria data are shown in Table 10.

Table 9. USES OF PHASE EQUILIBRIA DATA (8)

AREAS OF APPLICATION:

- Sintering of Ceramics - 117
- Search for New Compounds - 93
- Glass Processing - 63
- Education - 57
- Electronic Materials - 54
- Crystal Growing - 51
- Metal Coating or Processing - 41
- Smelting and Refining - 39
- Geology - 33
- Energy Conversion - 31
- Optical Materials - 29
- Magnetic Materials - 29
- Building Materials - 23
- Environment Effects - 1
- Nuclear Materials - 15
- Other - 19

Table 10. AREAS OF APPLICATION OF PHASE EQUILIBRIA (8)

Other: 19

Industry

1. Slagging reactions
2. Slags and high temperature properties
3. Refractory specialities
4. General reference
5. Reactions among various components in contact with each other
6. Catalysis research
7. Dental porcelain, fluxes, etc.
8. Refractories

University and Non-Profit Laboratories

9. Solid state chemistry
10. Class assignments
11. Prediction of defect structures
12. General Research
13. Solar Energy Materials

Table 10. AREAS OF APPLICATION OF PHASE EQUILIBRIA (8) - Continued

Government and National Laboratories

Unidentified

14. Refractory application

Foreign

15. Solid state inorganic reactions
16. Refractories
17. Ceramic composites
18. Search for application of poorly known minerals
19. Refractories
20. Understanding chemistry of firing of clays, non-metallic minerals and mixtures thereof

Question nine, requesting specific application of phase equilibria data, elicited 127 responses. This may perhaps be the most important point in the questionnaire and a complete listing of these answers is given in Appendix 2. The answers are listed by user categories and the numbers represent an arbitrary system of identification to protect the respondent's anonymity. Table 11 is an attempt to summarize each of these answers according to the type of material, the property of interest and the industry or product involved and Table 12 is a more concise statement of those applications listed by industrial sources. One typical quote suffices to illustrate the simple yet very important uses which can be made by easy access to phase equilibria data:

> "Refractory attack occurred at bottom of furnace when metal temperature was lowered 50°C. Analysis of phase diagram showed that 50°C drop lowered bottom of furnace operating temperature below melting point of anorthite which built up during low end of temperature cycle. Upon heating to upper end of metal melting temperature, corrosive liquid was formed which ate the SiO_2 lining of the induction furnace. Bottom end of temperature range was raised 50°C and problem was eliminated."

Table 11. SPECIFIC APPLICATIONS OF PHASE EQUILIBRIA DATA (9)

Material	Property	Industry or Product
	Industrial	
(1) Phosphates	ion exchange	Glass
Fluorides & silica	opacity	"
(2) Glass	optical, primary phase	Glass
(4) Alumina sources	melting points	Glass
(6) Slags + refractories	slagging reaction	Refractories
(7) Phosphates + sand	bonding	Foundry casting
(11) Glass and refractories	liquidus, bonding	Spark plugs
(12) $MgO-Al_2O_3-SiO_2$	refractory	Refractories
(13) Refractory + metal + slag	melting	Steel
Dolomite + slag	fluidity	"
Zirconia refractories	refractory	"
(21) Ni + Fe + silicates	solubility	Glass
(22) Al_2O_3, SiC	hardness	Abrasives
(23) Non-Metallics	phase identity	Mining
(26) Glasses	phase analysis	Electronics
(29) MgO-refractories	equilibrium	Glass
(30) Metal + slag + refractory	corrosion	Iron and Steel
(37) Metal + ceramic	brazing	Metalizing ceramics
(39) Silicates + nitrides and/or carbides	hardness	Abrasives
(41) Refractory + melt	corrosion	Glass
(42) ---	melting point	Electronics
(44) Arsenates	crystal growth	---
(46) Ceramics	semiconductivity	Opto electronics
"	melting points	"
"	phase analysis	"
(48) Titanates	semiconductivity homogeneity and phase stability	Communications
(49) MgO + cordierite	phase analysis	Automobile, Catalytic Converters
(51) Glass + refractory	liquidus, phase analysis	Glass

Table 11. SPECIFIC APPLICATIONS OF PHASE EQUILIBRIA DATA (9) - Continued

Material	Property	Industry or Product
	Industrial (Continued)	
(186) Alloys and glasses	glass properties	Refractories
(58) Refractory + metal	liquidus	Steel
(59) Tin + oxides	oxidation/reduction	Chemical
(60) Lithium compounds	general properties	Chemical
(63) Thermisters	phase analysis	Electronics
(69) Oxides	phase identification	Chemicals
(70) Ceramics	liquidus	Gas Turbine
(73) ---	melting	Refining
(75) Refractory Silicates	corrosion	Smelting
(76)	(Literature Survey)	
(77) ---	heat exchangers, catalysts, cement and concrete additives	Chemical
(78) β-Al_2O_3, nitrides	phase analysis	Smelting and Refining
(79) Low melting oxides	glass forming properties electronic properties	Glass
(86) Refractories	refractory nature, chemical reaction, homogeneity	Refractories
(92) ---	liquidus	Electronics (Glass)
(96) Refractory + slag	chemical reaction	Refractories
(99) Glass + ceramic	melting point	Electronics
(104) Slags	pyrometallurgy	Smelting
(105) ---	crystal growth	Electronics
(107) Multicomponent oxides	sintering	Brass
(109) Cement + sulfates	phase identification	Cement
(121) Tantalates + tungstates	dielectric	Electronics
(123) Glass compositions	primary phases	Glass
(124) Glasses	glass forming regions	Electro optics
(126) Oxides	chemical reactions	Electronics
(131) Oxide ceramics	eutectics	Refractories
(133) Glass	phase separation	Ceramics

Table 11. SPECIFIC APPLICATIONS OF PHASE EQUILIBRIA DATA (9) - Continued

Material	Property	Industry or Product
	Industrial (Continued)	
(137) ---	phase identification	Magnetics
(147) Clay, feldspar, refractories	phase identification	Refractories
(153) ---	material compatibility	Electronics
(155) Ceramics	phase formation	Fabrication
(159) Low temp. glasses	optical and electronic prop.	Electronics
(160) Ceramics	phase identification, thermal stability	Ceramics
(163) Ash-slag-ceramic	Chemical reaction	Gasification
(168) Slag-brick-low temp. melts	phase composition, sintering	Refining
(171) Raw materials	phase information	Glass
(175) Ceramic powders	flame spraying	Fabrication
(181) Glass	glass formation	Glass
(184) ---	extent of solid solution	Communications
	University and Non-Profit Laboratories	
(8) Oxides and silicates	crystal growth	Chemistry
(9) Minerals	rock formation	Geology
(14) ---	glass formation	Physics
(19) ("Dumb question - too vague")		
(25) Zinc phosphate	---	Ceramics
(33) Ceramics	precipitation	Materials Science
(35) Oxides	metastable equil., liquidus	Materials Science
(40) Slags and fluxes	welding	Mining
(47) Ceramics	phase transformations	Ceramics
(52) Refractory castables	melting point	Materials Science
(57) Oxides-slag	phase relations	Materials Science
(61) Oxides	stoichiometry, crystal growth	Ceramics
(65) ---	primary phases	Ceramics
(67) (Research)		Materials Science
(83) ---	sintering	Materials Science

Table 11. SPECIFIC APPLICATIONS OF PHASE EQUILIBRIA DATA (9) - Continued

Material	Property	Industry or Product
	University and Non-Profit Laboratories (Continued)	
(88) Ceramics	educational	" "
(91) Castable ceramics glasses, niobates, fluorides	immiscibility	" "
(98) Complex silicates	origin of magma	Geology
(102) Low temp. melts	eutectic temp.	Research
(108) Electrodes and insulators	phase composition	Materials
(113) ---	chemical compatibility melting points	"
(120) Refractories - slag	corrosion	"
(129) Slags - silicates	primary fields	Metallurgy
(136) Metal-oxides	chemical reactions	Metallurgy
(142) Oxides	phase relations	Semiconductors
(148) Ceramics	compound formation, phase transitions, solid solution	Materials Research
(164) Slag vs refractory	melting point, viscosity	Ceramics
(174) Minerals	formation of rocks	Geology
(183) Glass	glass melting, crystallization	Ceramic Engineering
	Government and National Laboratories	
(28) ---	geochemistry	Space
(66) Inorganic chemicals	container materials	Atomic Energy
(80) Oxides, chlorides	synthesis and sintering	B. Mines
(125) Oxides + flux	crystal growth	Physics
	Unidentified	
(3) Refractories + glass	chemical reactions	Glass
(55) Refractories + glass	chemical reactions	Refractories
(62) ---	compound formation	Non-Metallic Materials

Table 11. SPECIFIC APPLICATIONS OF PHASE EQUILIBRIA DATA (9) - Continued

Material	Property	Industry or Product
	Unidentified (Continued)	
(85) Glass	primary phase	Glass
(128) Zirconates and stannates	compound formation	Electronics
(157) Quote from F. N. Rhines, Ph. Diag. in Metallurgy, 1956		---
(170) Glass	liquidus, eutectics	Glass
(176) Glass-metal	temperature information	Materials
	Foreign	
(9) Metals-ceramics	compatibility	Research
(144) Refractories	Degradation, compound formation	Concrete
(89) Slag + refractory	chemical attack, sintering	Ceramics
(93) Metal-slag	phase relations	Steel
(97) Fluorides, silicates	eutectics, solid solution	Aluminum
(156) ---	liquidus temp., primary phases	Glass
(145) Fireclay	liquid temp.	Refractories
(178) Refractory + slag	corrosion	Ceramics
(127) Silicates, nitrides	liquid content	Ceramics
(87) Refractory + glass	corrosion	Glass
(112) Metal-oxides-nitrides	eutectics	Metals
(154) Raw materials	economics of heat treatment	Non-Metallic Minerals
(167) Cements	sintering, liquidus	Non-Metallic Minerals
(146) Slag	slag property	Building Materials
(182) ---	chemical reactions	Electronics
(71) ---	glass forming regions	Research
(116) Refractories	research	Refractories
(165) Nuclear materials	phase transformation	Nuclear Materials
(82) Fly ash	phase formation	Research
(140) Glass and slag	synthesis, devitrification	"
(100) ---	crystal growing	Electronics
(138) Glass	melting	Glass
(150) ---	energy conversion	Solar Research
(173) ---	melting temp., compound formation	Engineering Materials
(172) Slag + ore gangue	liquidus temp.	Metallurgy

Table 12. SPECIFIC APPLICATION OF PHASE EQUILIBRIA DATA (9)

Total Number of Answers - (127)

Industrial - (67)

MATERIAL

Oxide Ceramics (12)	Silicates (4)
Glass or Slag Plus Refractory (10)	Alumina (3)
Glass or Slag (9)	Metal + Slag (3)
Refractories (6)	Titanates, Etc. (2)
	Raw Materials (2)

PROPERTY

Identification of Phases (17)	Corrosion (4)
Glass Forming Regions (9)	Homogeneity (4)
Melting Points (6)	Chemical Reaction (4)
Liquidus (5)	Primary Phases (3)
Sintering (4)	Refractory Nature (3)

INDUSTRY

Glass (12)	Chemical (4)
Electronics (9)	Refining and Smelting (4)
Refractories (7)	Ceramics (2)
Electro-Optics (5)	Communications (2)
Iron and Steel (5)	Abrasives (2)

3.2.2 Classes of Systems of High Interest (10)

Question ten asked, "Which classes of systems are of high interest to you? Please indicate by 3 = High interest, 2 = Moderate interest, 1 = Some interest, 0 = No interest." Most respondents listed only 3 and 2. Table 13 lists the classes of systems divided into oxides, halides and general with the number of (3) answers given for each class, rearranged according to those of most interest in each category. Metal oxides and silicates are obviously of the highest interest with oxides in general being the most important. In the general category there is a significantly large vote for carbides and borides which are not covered in the present compilation, nor are there plans for inclusion of them. At the bottom of this list are arsenides, phosphides, selenides, and tellurides which are also not intended for coverage in the near future. Fifteen respondents (8%) checked the category "Other [please specify]" and their specified systems of interest are shown in Table 14.

Table 13. CLASSES OF SYSTEMS OF HIGH INTEREST (10)

OXIDES	NO.	(%)	GENERAL	NO.	(%)
Metal Oxides	144	(77)	Carbides, Borides	43	(23)
Silicates	107	(58)	Oxynitrides, Nitrides	32	(17)
Alkali Oxides	77	(41)	Sulfates, Sulfides	32	(17)
Alkaline Earths	53	(28)	Carbonates	31	(17)
Rare Earths	40	(22)	Nitrates and Nitrites	18	(10)
Phosphates	35	(19)	Aqueous Systems at 1 atm	14	(8)
Borates	34	(18)	Hydrothermal Systems	12	(6)
			Arsenides, Phosphides	10	(5)
HALIDES	NO.	(%)	Selenides, Tellurides	6	(3)
Fluorides	25	(13)			
Chlorides	24	(13)			
Bromides	1				
Iodides	1				

Other - 15 (8)

Table 14. CLASSES OF SYSTEMS OF INTEREST (10)

Other: 15

Industry:

1. Ferrous metals and pyrometallurgical slags in contact with refractory oxides and silicates, molten metallurgical slags as such and in contact with molten metals
2. Metals - Sn, Fe, Mo, Si and Pt
3. All of interest at one time or another
4. Compounds in the $A_xB_yC_z$ class
5. Any and all properties of tin and tin oxides
6. Thick film conductor systems, transparent semiconducting oxides: SnO_2, In_2O_3-nonstoichiometric, SnO_2-In_2O_3-O, Sn, In
7. Alumino-silicates
8. Metals and metal systems

University and Non-Profit Laboratories

9. High pressure silicate systems to ~60 kb
10. Systems at high pressure
11. Ternary and quaternary oxides, carbides and nitrides
12. Nitrides
13. Silicides
14. Common alloys

Government and National Laboratories

Unidentified

15. Combustion of sulfides is of increasing interest
16. Metals, polymers

Foreign

17. Silicates and waste out temp. >500° mainly >1000°K

3.3 Evaluation of Phase Diagrams for Ceramists as a Publication of the American Ceramic Society (III)

In general the tone of evaluation in this section was very favorable, although it might be argued that the audience was biased in favor of the book as they had just ordered the latest supplement.

3.3.1 Value of Phase Diagrams for Ceramists as a Publication (11)

As shown in Table 15, an overwhelming majority (87%) considered "Phase Diagrams for Ceramists" very valuable; defined as "in the top priority category among special publications [Note: The Journal, Bulletin and Ceramic Abstracts are not special publications]". There were no votes for the category "No Value; should be discontinued".

Table 15. EVALUATION OF PHASE DIAGRAMS FOR CERAMISTS (11)

- Very Valuable - 162 (88%)
- Moderately Valuable - 20 (11%)
- Marginal Value - 1
- No Value - 0

3.3.2 Does Range of Systems Treated Span Range of Interest (12)

Question (12) asked: Considering the 1975 Supplement together with the 1969 Supplement and the 1964 volume, does the range of systems treated span your range of interests? This question elicited answers similar to those of question 10. Indeed, there was a large amount of redundancy deliberately built into the questionnaire specifically to obtain that opinion which most interested or bothered the respondent. In this category 126 or 68% of the respondents checked YES, indicating they were quite happy with the range of coverage. Only 38 or $\sim$20% answered NO and bothered to describe other systems which should be covered. Their answers are given in Table 16 and summarized in Table 17. Some of the suggested systems summarized under "not covered" are of course found in other non-ceramic compilations. Also note the similarity to the answers for question 19.

In Table 17 and succeeding tables the figures in brackets after the information refer to the number of times it was suggested. No number means it was only mentioned once. Unfortunately, the answers reflect the systems which the respondents want studied rather than compiled. There is very little published data in many of the categories listed. Many of the desired categories are outside the field of present coverage. Indeed some of them are outside the field of ceramics entirely. Other answers have nothing to do with the question; for instance, the comments "total coverage not adequate" and "time lag too great". These later points will be covered in the conclusion section.

Table 16. OTHER SYSTEMS WHICH SHOULD BE COVERED (12)

1. Hydrates; more on phosphates (also boro-phosphates)
2. ZrO_2-SiO_2, ZrO_2-SiO_2-Al_2O_3. Fe (molten metal) with a wide variety of commercially important refractory oxides, silicates and mixtures thereof, and under reducing through oxidizing environments
3. CaO-Al_2O_3-B_2O_3
4. Would like more information on glass forming compositions
5. Sn-oxygen up to at least 1100°C, Sn-SnO (SnO_2)-Al_2O_3, SiO_2 and ZrO_2; Sn-SnO_xFe (Fe_nO_m), Sn-sodium silicates, Sn-SiO_2-Na_2O-SO_2
6. Carbides, borides, nitrides
7. Carbides, borides and nitrides should be included
8. Coverage not adequate - should be complete - wide ranging
9. Mixed systems - solid state devices (electro-ceramics)
10. Silicides would also be useful
11. Simple metal systems
12. Intermetallics
13. SnO-O, SnO-SnO_2, SnO_2-O, SnO-CaO-FeO-SiO_2
14. Nitrides-oxynitrides, Al_2O_3-AlN, Si_3N_4-SiO_2-Y_2O_3
15. More double oxide systems - $BaTiO_3$-$SrTiO_3$-$CaTiO_3$
16. Mixed systems oxide-nitride, oxide-carbide
17. More on nitride systems
18. More information on transmission oxide systems - nonstoichiometric SiO_{2-x} - silicon nitride systems
19. Most combinations of silicates, borates and oxides
20. Mn-Ni-Co oxides - thermistors, Bi-Pd-O, Bi-Ag-O
21. Low temperature solder glass, attaching Al_2O_3 to Al_2O_3
22. Absolutely no information on a large number of minerals especially sulfide, sulfates and ore minerals - see Dana
23. Enlarge sections on hydrated minerals and high pressure
24. Need more high P, P-T diagrams
25. Sulfides, selenides, tellurides
26. Metal-alkali, etc., nitrides, borides, carbides, silicides and oxynitrides
27. Carbides, nitrides, etc.
28. One special interest relates to ternaries among NiO-ZnO-MnO-CoO-FeO-Fe_xO_4 type materials
29. Would like to see a "complete" compilation in future

Table 16. OTHER SYSTEMS WHICH SHOULD BE COVERED (12) - Continued

30. Little on non-oxygen containing systems given. Would like more on borides, carbides, etc.
31. More up-to-date information needed, time lag too great
32. More on sulfides and other chalcogenides and pnictides
33. NiS/ZnS, CrO_x/C, As/O_2, CrO_x-oxide
34. Common alloys, metal-oxygen, metal-H, metal-N_2, etc.
35. Could cover ZrO_2 in more detail
36. Nitrides and carbides
37. Metals
38. Th-W-O (reference enclosed)
39. Oxy-fluoride systems
40. Insufficient detail on such as ZrO_2 ternary systems
41. Addition of nitrides would be valuable
42. Bi_2O_3-TiO_2-alkali oxides
    Bi_2O_3-Nb_2O_5-alkali oxides
43. Nitrides-oxynitrides-carbides-borides

Table 17. OTHER SYSTEMS WHICH SHOULD BE COVERED (12)

ALREADY COVERED	NOT COVERED
Glass Forming Systems (4)	Carbides, Borides, Nitrides (7)
Refractories (3)	Mixed Systems (5)
High Pressure (2)	Selenides, Tellurides (2)
Sulfides (2)	Silicides
Electronic Oxide Materials	Simple Metal Systems (2)
Oxyfluorides	Intermetallics
Hydrates	Metal-Gas Systems
Minerals	Refractories with Molten Metal
	Non-Oxide Containing Systems

IMPORTANT COMMENTS:

Systems with Variable P_{O_2} (8)

Total Coverage Not Adequate

Time Lag Too Great

3.3.3 Evaluation of Phase Diagrams for Ceramists (13-16)

In this section the respondent was asked to comment on (13) Gaps in Coverage, (14) More Attention During Experiment, (15) Is Information in Useful Format and (16) Are (1975) Commentaries Useful and of Right Length. The completely satisfied respondent would answer No, No, Yes, Yes, About Right to these questions. Table 18 shows the statistical summary of these answers and again it is evident that most people are fairly satisfied with the book as presently published.

Table 18. EVALUATION OF PHASE DIAGRAMS FOR CERAMISTS (III)

(Completely Satisfied Checks No, No, Yes, Yes, About Right)

(13) Gaps in Coverage - No - 93
Yes - 67

(14) More Attention During Experiment - No - 89
Yes - 69
I Don't Know - 1

(15) Information in Useful Format - Yes - 165
No - 10

(16) (1975) Commentaries Useful - No - 7
Yes - 153

LENGTH: Too Long - 7
About Right - 129
Too Short - 9

3.3.3.1 Gaps in Coverage (13)

Table 19 shows the answers of 67 respondents who considered that there were gaps in coverage. Their written descriptions, summarized in Table 20, again show that the gaps are mostly in the availability of experimental data rather than in the compilation of published data.

Table 19. GAPS IN COVERAGE (13)

Industrial

1. $K_2O-P_2O_5$
2. Metastable and stable liquid-liquid immiscibilities
3. Low temperature phosphate phases
   Water containing glasses
4. ZrO_2-SiO_2-MgO, $ZrO_2-SiO_2-Al_2O_3$
5. Metastable phases should be delineated
6. Al_2O_3-binaries
7. More data on hydrous systems
8. Nitrides, borides and carbides
9. High pressure systems; example $Al_2O_3-SiO_2$
10. Nonequilibrium situations
11. Rare earths - 2
12. Sulfides, phosphates, arsenates not complete
13. Noble metal compounds; example noble metal oxides-binary oxides
14. Rare earth oxides need (non R.E.) purity analysis
15. $SrO-CaO-MgO$ in $LaCrO_3$
16. Standard refractories vs active oxides which lower useful life
17. Vapor pressures for depositing ceramic phases
18. More oxide-oxide and oxide-metal diagrams
19. ZnO-metal oxide systems with low concentration metal oxide
20. More on $BaTiO_3$-additives used in capacitors
21. Basic ceramic silicate systems from Vol I given commentaries as found in Vol III
22. Compilation not complete probably because only a selected number of journals are surveyed.
23. Low temperature solder glasses
24. S, Se, Sb, As assemblages pertaining to minerals
25. $CaO-ZrO_2-SiO_2-R_2O_3$ group
    P_{O_2} variation in $CaO-ZrO_2-SiO_2-R_2O_3-RO$
26. Complex systems containing SnO and SnO_2

University

27. Sulfides, selenides and tellurides
28. More ternaries
29. Many diagrams are incomplete, especially ternaries
30. Metal-gas systems (like Fe-O)
    Phosphate systems
    Complex systems, B.O.F.-steel slags
31. $CaF_2-CaO-FeO-SiO_2$ (steelmaking slags) - up to 10% CaF_2
32. Metastable silicate systems

Government and National Laboratories

33. $Li_2O-MgO-Al_2O_3$, $LiCl-MgCl_2-AlCl_3$
34. Multicomponent oxides

Table 19. GAPS IN COVERAGE (13) - Continued

Unidentified

35. More quaternary information
36. Sulfides, nitrides and other non oxides
37. $SiO_2-GeO_2-B_2O_3$, $SiO_2-P_2O_5-B_2O_3$ and other systems for optical wave-guides

Foreign

38. Binary solid solutions
39. ZrO_2-SiO_2, Al_2O_3, P_2O_5, FeO, Fe_2O_3
40. Nitrides, oxynitrides, carbides
41. High pressure systems, hydrothermal systems
42. $CaO-Al_2O_3$, $CaO-P_2O_5-H_2O$, ferrites (cubic + hex.)
43. Actinide oxide systems - esp. hypostoichiometric
44. Published diagrams not (yet) included

Table 20. ARE THERE GAPS IN COVERAGE OR COMPILATION (13)

No - 93

Yes - 67

Summary of Answers

- Multicomponent Oxides - 34
- Systems with Variable P_{O_2} - 17
- Non Oxides - 14
- Hydrous, Hydrothermal and High Pressure - 5
- Metastable and Non-Equilibrium Phases - 3
- Commentaries for Important Systems from Vol I and II
- Compilation not Complete Because Some Published Diagrams not Included

3.3.3.2 Experimental Needs (14)

Question 14 asked "Are there features of the systems to which more attention should be given during experimental studies [such as solid solution below the one percent level]?" Only 18 people , or about 10%, specifically agreed with the suggestion concerning solid solution below the one percent level. They were about equally divided between industrial and university representatives. As pointed out by one individual in charge of the Materials Research Laboratory of a leading U.S. university, "This is very difficult data to get." The descriptions to the Yes answers of 69 individuals (37%) are given in Table 21 and summarized in Table 22 according to the type of applications of the features. Once again the answers are not necessarily those which have much relation to the question.

Table 21. MORE ATTENTION DURING EXPERIMENTAL STUDIES (14)

Yes (69)

Suggested: Solid solution below the one percent level (18)

1. Effect of SO_4^{-2} on glass melting
2. Molten metals in contact with refractories and slags
3. Mixed oxides
4. Kinetics
5. Enlargements to show details: e.g. - a peritectic
6. Precipitation of heterogeneous phases in mixed systems (Exsolution)
7. Ranges of homogeneity
8. X-ray lattice parameters vs composition in solid solution
9. Silicides
10. Rates of transformation
11. Viscosity information (even qualitative)
12. Temperature information on ternaries
13. Glass forming regions - more property measurements
14. CaO in MgO
15. Na_2SO_4-Al_2O_3-SiO_2
16. SiO_2-metals, SiO_{2-x}-Si, Si-Na_2O-SiO_2-metals, metal oxides
17. Impurity effects
18. More detailed attention to possible Magnelli-type phases
19. Stable glass forming regions
20. B_2O_3 and CaO in MgO at <1% level
21. Opinions from experts on relative accuracy of conflicting published data
22. Metastability and attainment of equilibria
23. Kinetics of precipitation - purities of starting materials
24. More information on immiscibilities
25. Solid solution ranges
26. Effect of P_{O_2} on equilibria and solid solution. Extrinsic vs intrinsic behavior (impure systems vs purity)
27. Oxidation state
28. Activity data, % solid solution, oxygen partial pressure, nonstoichiometry
29. Suggested <1% ss is "Very Difficult Data to Get"
30. Phase changes, metastable high temp. phases $\alpha,\beta,\gamma,\delta,\theta$ - Al_2O_3
31. P-T-X equilibria including vapor phase
32. Sub-solidus
33. Oxidation potential of atmospheres
34. Solid solution
35. Metastability of technological interest
36. Glass forming regions
37. Diagrams are more believable with ss information
38. Homogeneity range of transition metal oxides
39. Slag and other wastes plus feldspar, petolite, etc.
40. Crystallographic information on solid solutions
41. Influence of impurities (due to gaseous absorption)
42. Results of ΔFP-T studies
43. ss and method of detection of ss

Table 22. ARE THERE FEATURES WHICH NEED MORE ATTENTION DURING EXPERIMENTAL STUDIES? (14)

No - 89 (48%)

Yes - 69 (37%)

APPLICATIONS:

PRIMARY	EITHER	SECONDARY
Glass Forming Regions (3)	Ranges of Homogeneity (5)	Effect of P_{O_2} on Equilibria (5)
Viscosity (Even Qualitative)	Impurity Effects (5)	P-T-X Equilibria and Vapor Pressure (2)
SO_4^{-2} in Glass	Kinetics (3)	Phase Changes
Molten Metals vs Refractories and Slag	Metastability (2)	Crystallographic Information
Slag and/or Other Wastes Plus Feldspar, Clay, etc.	Lattice Parameters vs Composition	Magnelli-Type Phases
More Property Measurements	Immiscibility Regions	Nonstoichiometry
	Exsolution	Methods of Detection of Solid Solution

"Opinions from Experts on Relative Accuracy of Conflicting Published Data"

3.3.3.3 Useful Format (15)

A total of 165 respondents agreed that "the information given in the diagrams (was) presented in a useful format." Although only 10 persons indicated a No answer there were considerably more suggestions made for possible improvements. These suggestion are given in Table 23 and summarized in Table 24.

Table 23. IS INFORMATION IN DIAGRAMS IN USEFUL FORMAT? (15)

Yes - 165 No - 10

1. Some exotic formats should have simplified more routine format as well.
2. An abstract published with data would be useful.
3. The 1975 (format) is well done.
4. Always state whether mole or weight percent.
5. Axes should always be mole % rather than wt %.
6. More isothermal sections and joins in ternary systems
7. Better cross-referencing, i.e. ternary liquidus to binary subsolidus
8. Larger size
9. More use of other descriptive methods
10. Oxygen partial pressure of atmosphere implicity assumed to be that of air
11. Large-scale diagrams are also useful
12. All diagrams should be reviewed for theoretical correctness
13. Diagrams in earlier volumes difficult to follow
14. Often too little format

Table 24. IS INFORMATION IN PHASE DIAGRAMS IN USEFUL FORMAT (15)

1. The 1975 Format is Well Done (6)
2. State Whether Mole or Weight Percent (4)
3. Axes Should Always be Mole % not Wt %
   (Axes Should Always be Wt % not Mole %)
4. More Isothermal Sections (2)
5. Better Cross Referencing
   i.e. Ternary Liquidus to Binary Subsolidus
6. Exotic Formats Should Have Simplified Formats as Well
7. More Use of Descriptive Methods
8. P_{O_2} Assumed to be Air
9. All Diagrams Should be Reviewed for Theoretical Correctness

3.3.3.4 Information in Commentaries (17)

The respondents were asked to check four informational points (purity, accuracy, method and reference) as to their usefulness in the commentaries by using 3 = High value, 2 = Moderate, 1 = Marginal, 0 = No value. No one bothered to indicate zero value although certain portions were often without an entry. Table 25 indicates the number of times each of these points were given a 3 (High value). Purity of starting materials was considered to be the most important single factor to be included.

Table 25. IS IT USEFUL TO HAVE INFORMATION IN COMMENTARIES ON THE FOLLOWING: (17)

High Value:

Purity of Starting Materials - 103 (55%)

Information on Accuracy - 88 (47%)

Description of Method - 85 (46%)

References to Earlier Work - 61 (33%)

3.3.4 Additional Information for Commentaries (18)

Question 18 asked "What additional information, if any, would you suggest be included in the diagrams and/or the commentaries" and gave four blank lines for an answer. Only 43 people (23%) bothered to answer this question, and again, many answers, as listed in Table 26, had little bearing on the question. Tables 27 and 28 summarize the answers according to those possibly within the scope of the compilation, and those probably outside the scope of the compilation. In Table 29 four comments are given from answers to question 18 which are well worth considering, if not for inclusion in the commentaries, at least as a starting point for discussion.

Table 26. ADDITIONAL INFORMATION NEEDED (18)

1. Same information in same order for commentaries
2. Use wt% exclusively (!)
   Identify mol % or wt %
   Commentary on converting mole % to wt %
3. Authors feeling of accuracy of their work
4. More information on oxide stoichiometry
   high pressure diagrams - diamond - boron nitride
5. X-ray data for phases - reference to powder diffraction file
6. a) Effect of impurities (normally occurring)
   b) Effect of added impurities
7. Prefer return to '69 format - have good library

8. Identify crystalline vs amorphous
   Indicate if solid state diffusion starts phase change or compound formation or if partial melting is necessary
   Include precious metal-base metal oxide systems
9. '75 format is commendable
10. Vapor pressure, electrical resistivity, dielectric constant, optical properties, mechanical properties
11. Iso-activity plots for liquid oxide systems
12. The more the better
13. References
14. Experimental difficulties with vaporization or low reaction rates useful for practical use of phase diagrams
15. Information supplied is adequate
16. As much as possible
17. Metastable phases - potential problems such as volatilization
18. None - keep up good work
19. Chalcogenide glasses with their properties, low temperature solder glasses
20. Give title of reference
21. A list of what optical/structural/physical data are available in the source reference
22. Does proposed diagram violate phase rule?
23. Bibliography including titles
24. Identify which part of diagram is theoretical and which is experimental
    Conditions of experimental work - oxidizing, reducing-inert atmosphere
25. O.K. as is
26. Free energy data - elements and compounds
27. More complete coverage
28. Hansen format useful - much more information makes volume cumbersome
29. Critical comment on possible errors in original work
30. Compilation of electronic properties
31. Tabulation of invariant points
32. Purity, accuracy, methods and reference as in question (17)
33. Reaction rates - viscosity of liquids
34. Useful data

Table 26. ADDITIONAL INFORMATION NEEDED (18) - Continued

35. Glass forming regions - glass properties, refractive index, glass-transition temperature
36. Reaction kinetics
37. References to earlier work and conflicting data
38. References to x-ray data for identification of phases
39. Commentary on attainment of equilibrium (rate) ferrostress of metastable phase - indication of probability of real system attaining equilibrium diagram phase composition
40. Original aim of the work. Reaction rates
41. Comparison with earlier work
    Comments on value of earlier published diagrams
42. Purity of starting materials
43. More details on foreign publications,
    Regions of glass formation
44. Scale of composition of the individual components

Table 27. WHAT ADDITIONAL INFORMATION SHOULD BE INCLUDED? (18)

Return to '69 Format - (1)

Keep '75 Format - (9)

Answers Possibly Within Scope of Compilation

References (with titles) to Earlier Work (5)

Reaction Kinetics (4)

Purity (3)

References to X-Ray Diffraction Data (2)

Accuracy (2)

Stoichiometry

Metastable Phases (2)

Volatilization (2)

Comments on Possible Errors

More Complete Coverage

Table 28. <u>WHAT ADDITIONAL INFORMATION SHOULD BE INCLUDED (18)</u>

<u>Answers Probably Outside Scope of Compilation</u>

- Glass Forming Properties (3)
- Optical Properties (2)
- Vapor Pressure
- Electrical Resistivity
- Dielectric Constant
- Mechanical Properties
- Free Energy Data
- Electronic Properties
- Viscosity of Liquidus

"Useful Data"

Table 29. <u>WHAT ADDITIONAL INFORMATION SHOULD BE INCLUDED (18)</u>

<u>Noteworthy Comments:</u>

1. <u>Same</u> Information in <u>Same</u> Order for Commentaries
2. A List of What Kind of Optical-Structural-Physical Data are Available in the Source Reference
3. Identify Which Part of Diagram is Theoretical and Which is Experimental
4. Comment on Rate of Volatilization and Attainment of Equilibrium to Indicate Probability of Real System Attaining Equilibrium Phase Composition

3.4 Important Needs for Experimental and/or Theoretical Work (IV)

In section IV of the questionnaire the respondent was asked to comment on "important needs for experimental and/or theoretical work not now being done". It was pointed out that "Compilers are usually also research workers and influence other workers. Your indication of the relative importance of certain research gaps might lead to filling some of these gaps". In general the response was very good. In fact, one respondent eloquently answered, "General increase in information on phase diagrams is needed. This is basic information of lasting value".

3.4.1 Specific Systems for Which Diagrams are Needed (19)

Question 19 asked "Are there specific systems for which diagrams are needed and not available?" There were 44 No answers and 90 Yes answers. In describing their Yes answers the respondents were generally quite specific and these specific needs are listed in Table 30. These answers have been summarized in Table 31 by types of systems, by applications or in special categories. Note that the types of systems include most of those listed in question 10 and the applications cover most of those mentioned in question 8.

Table 30. SPECIFIC SYSTEMS FOR WHICH DIAGRAMS ARE NEEDED (19)

No - (44) Yes - (90)

1. In_2O_3, SnO_2, Cr_2O_3, - silicates NiO with Na and K alumina-silicates
2. Off stoichiometric effects in solid state and abrasives
3. Na_2O-Li_2O-P_2O_5
4. CaO-Al_2O_3-B_2O_3
5. Nitrides: Be-Si-N_2, Mg-Si-N_2
6. Al_2O_3-SiO_2-(SO_3), NaO_3-SiO_2-Na_2BO_3
7. Mixed systems with semiconducting properties
8. All diagrams possible
9. CuO-Al_2O_3
10. BaO-TiO_2 with Nd, Sm, Pr oxides
11. Na_2O-Li_2O-Al_2O_3, Si_3N_4-MgO-Al_2O_3, Si_3N_4-Y_2O_3-Al_2O_3
12. V_2O_5-PbO-P_2O_5, V_2O_5-ZnO-P_2O_5
13. Si-O-N, β-Al_2O_3 (Na, Li)
14. Nitrides
15. V_2O_5-Al_2O_3-SiO_2 and V_2O_5-Al_2O_3-P_2O_5-SiO_2
16. FeO-ZnO-SiO_2
17. Garnets
18. ZnO-metal oxides
19. Refractory oxide - metal oxide, ZnO-metal oxide
20. Ferrites
21. SiO_2-Al_2O_3-CaO-B_2O_3; SiO_2-Al_2O_3-CaO-CaF_2
22. SiO_2-B_2O_3-alkali oxides - alkaline earth oxides
23. Mn-Ni-Co-Cu-O
24. Rare earth oxide systems
25. SiO_2-Al_2O_3-B_2O-CaO; TiO_2 - transition elements, CaO, MgO, etc. - SiO_2-Al_2O_3-B_2O_3-Na_2O

Table 30. SPECIFIC SYSTEMS FOR WHICH DIAGRAMS ARE NEEDED (19) - Continued

26. $ZnO-Bi_2O_3-TiO_2$, Sb_2O_3, Co_3O_4
27. Low temperature solder glasses
28. Ore minerals and assemblages Au, Ag - Se, Te
29. Zirconates, titanates, niobates, stanates and combinations
30. CeO_2-other oxides
31. $SnO-SnO_2$-silicates
32. $SiO_2-AlN-Y_2O_3$
33. Multicomponent silicates
34. Sulfides, selenides, tellurides
35. Simple oxides, i.e. Al_2O_3, MgO, CaO
36. $MgO-Y_2O_3-ZrO_2$ - other ternary zirconates
37. Rare earths-O-C-N system
38. Si-C, Si-C-N, Si-Al-O-N, $Na_2O-Al_2O_3-Li_2O$
39. Nitrides - SiN, TiN, ZrN
40. Complex glass, refractory systems, fluorides, rare earths, low P_{O_2}
41. High pressure silicates
42. $MgO-ZrO_2$, $MgO-Cr_2O_3$
43. Oxide-carbonate-sulfate
44. Nitrides: M-N-C-B-Si-O ternary and/or more complex
45. Nitrides, carbides
46. Metal-oxygen, i.e. (Fe-O)
47. Steelmaking - $CaF_2-CaO-FeO-SiO_2$
48. Metal oxides (Cr_2O_3, Fe_2O_3) with molten hydroxides
49. Cement $SiO_2-Al_2O_3-FeO_x-CaO-MgO$
50. Hydroxy-apatite-H_2O
51. $SiO_2-GeO_2-B_2O_3$, $SiO_2-P_2O_5-B_2O_3$
52. $CaO-MgO-SO_3$
53. Steelmaking components - refractory oxides
54. ZrO_2-ZrF_4, $ZrO_2-ZrF_4-Na_2O$ (Group I and II oxides)
55. Nitrides, silicides
56. Me-O-N, Me-N-C, Me-N, Me-C
57. High pressure systems
58. $SiO_2-Al_2O_3$-alkaline earth oxides - alkali oxides + other phases
59. Actinide oxide ternary systems
60. $PbO-PbF_2-SiO_2$, $PbO-PbF_2-P_2O_5$

Table 30. SPECIFIC SYSTEMS FOR WHICH DIAGRAMS ARE NEEDED (19) - Continued

61. Nitrides, borides, silicides, phosphides, carbides, chalcogenides

62. Metallic systems, borides, nitrides, carbides, silicates, phosphides, aluminides

63. $CaO-MgO-Al_2O_3$

Table 31. NEEDS FOR EXPERIMENTAL OR THEORETICAL WORK NOT NOW BEING DONE (IV)

SPECIFIC SYSTEMS FOR WHICH DIAGRAMS ARE NEEDED (19)

TYPES:

Silicates (9)	Carbides and Nitrides (9)
Aluminates (5)	Oxynitrides (6)
Zincates (5)	Sulfides, Selenides, Tellurides (3)
Rare Earths (4)	Fluorides, Oxyfluorides (3)
Phosphates (3)	Oxyhydroxides (2)
Zirconates (3)	Sulfates
Titanates (2)	Metal-Oxygen Systems
Stannates (2)	Ferrites
Vanadates (2)	Actinides
Borates	

APPLICATIONS:

Glass (7)

Magnetics (3)

Refractories (3)

Steel Making (2)

Cement

Abrasives

Semiconductors

Ferroelectrics

Electronics

Optics

Table 31. NEEDS FOR EXPERIMENTAL OR THEORETICAL WORK NOT NOW BEING DONE (IV) - Continued

SPECIAL CATEGORIES:

Ore Minerals

Low P_{O_2}

High Pressure Systems

High Pressure Silicates

Very Complex Systems
(Five or More Components of Mixed Types)

Oxy-Nitro-Carbides

Oxide-Carbonate-Sulfates

3.4.2 Existing Diagrams Which Need Updating or Correction (20)

Question 20 asked "Are there parts of existing diagrams for which more detailed data are needed or which you suspect of being in error?" There were 68 No answers and 42 Yes. The Yes answers are given in Table 32 and summarized by categories in Table 33. Many of these were silicates, aluminates or zirconates.

Table 32. ARE PARTS OF EXISTING DIAGRAMS IN ERROR OR NEED MORE DATA (20)

No - 68
Yes - 42

1. Phosphate, polyphosphate combinations with MnO, FeO, etc.
2. Cr_2O_3-SiO_2 (reliability)
3. Large Scale Diagrams - Na_2O-CaO-SiO_2, Na_2O-MgO-SiO_2, Na_2O-B_2O_3-SiO_2
4. K_2O-Al_2O_3-SiO_2
5. Specific diagram in error - reference given but not system
6. More property measurements needed
7. Standard refractory products
8. CaO-Al_2O_3-SiO_2
9. Na_2O-MgO-Al_2O_3-SiO_2 and K_2O-MgO-Al_2O_3-SiO_2
10. Al_2O_3-MgO, Al_2O_3-SiO_2
11. Low alkali oxide content - binary silicates
12. Al_2O_3-SiO_2 (mullite) MgO-Al_2O_3-SiO_2-CaO
13. Anorthite - albite (1 atm)
14. Many are based on assumed equilibrium

Table 32. ARE PARTS OF EXISTING DIAGRAMS IN ERROR OR NEED MORE DATA (20) - Continued

15. Many, Al_2O_3-SiO_2, CaO-ZrO_2
16. Oxides - silicates >1800°C, i.e. liquidus of 3CaO:SiO_2
17. MgO-SiO_2
18. Many diagrams only determined very accurately if need arises
19. Many diagrams from Russian sources
20. Na_2O-Al_2O_3
21. Chromates-hydroxides
22. High metal content nonstoichiometric oxides
23. Vapor pressure
24. CaO-ZrO_2
25. Al_2O_3-ZrO_2-SiO_2
26. SiO_2-Al_2O_3-alkaline earth oxides - alkali oxides - Anorthosite
27. Tl-S and other Tl-bearing systems
28. UO_{2+x}
29. Pb-O_2 and Pb-F_2
30. Bi_2O_3-TiO_2

Table 33. EXISTING DIAGRAMS WHICH NEED UPDATING OR CORRECTING (20)

No - (68)

Yes - (42)

CATEGORIES:

Silicates (14)	Sulfides
Aluminates (3)	Oxyfluoride
Zirconates (3)	Garnets
Titanates	Non-Stoichiometric Oxides
Chromates	Refractories
Phosphates	Ultra High Temperatures (>1800°C)
Uranates	

- Many Based on Assumed Equilibrium
- Many Determined Accurately Only if Need Arises

3.4.3 Aspects of Phase Equilibria Needed but Inadequately Explored (21)

Question 21 was worded, "Are there aspects of phase equilibria which are needed and generally inadequately explored in most studies? [for example, solid solution below one percent]" There were 61 No answers and 51 Yes. The Yes respondent was asked to "please describe the problem and, if possible, suggest experimental methods for obtaining such data". The descriptions given by the Yes respondents are given in Table 34. Fifteen people agreed with the example of solid solution below the one percent level as shown in Table 35, which also lists some other aspects given in the answers. In Table 36 a summary is given of some of the suggested experimental methods which might be used to obtain some of these hard to get data.

Table 34. ASPECTS OF PHASE EQUILIBRIA NEEDED BUT INADEQUATELY EXPLORED (21)

No	-	63
Yes	-	51

1. Effect of molar volume and thermal expansion on glasses
2. Kinetics - convey a feeling for kinetics of the system in the published article and include in commentary
3. Organic-inorganic phase diagrams
4. Influence of rate of cooling on physical form of precipitated (solid) phases, also composition of grain boundary phases
5. Effect of small amount of additives on melting points, solubilities, etc.
6. CaO in MgO
7. Special issue on impurities (dilute solid solutions)
8. Immiscibility gaps
9. Solid solution below 1%
10. a) Solid solution at all levels
    b) Explore more systems as a function of P_{O_2}
11. Systems fired in atmospheres other than air
12. Physical properties of phases formed
13. Microphase separation in glasses and coherent precipitation at or near boundaries
14. Time-temperature-transformation diagrams
15. Detect second phases in "single phase material" by TEM and electron diffraction (and lattice images)
16. Temperature - composition - P_{O_2} diagrams
17. Equilibrium in <u>ultra</u> high purity systems
18. Solid solution below one percent
19. Solid solution of ternary compounds by vapor pressure measurements across the solid solution region

Table 34. ASPECTS OF PHASE EQUILIBRIA NEEDED BUT INADEQUATELY EXPLORED (21) - Continued

20. a) Low P_{O_2} systems - high temperature x-ray in mixed gases

    b) Phase equilibria in "pure" systems may be result of impurity effects

    c) Resistivity vs temperature to determine intrinsic and extrinsic behavior

21. Metastable immiscibility of silicate liquids and immiscibility of silicate solid solutions below solidus

22. Solid solution below 1% by SEM and etch methods

23. Solid solution thermodynamics

24. More attention to the vapor phase

25. Some semiconducting oxides

26. Details of P_{O_2} dependence in systems involving transition metal oxides

27. Solid solution limits in binary diagrams

28. Neutron diffraction; (OH) contamination in oxides by IR; neutron activation analysis

29. Application of phase diagrams to non-equilibrium systems

30. Effect of trace impurities - full chemical characterization of starting material

31. Vapor pressure

32. Attainment of equilibrium

33. Different "types" of quartz having different solution rates in various melts

34. Solid solution below 1%,
    Vapor pressure at high temperature

35. Non-condensed system equilibria (UO_{2+x})

36. Solid solution below 5%

37. Solid solution below 1%

38. Systems containing vapor-liquid and vapor-solid

Table 35. ASPECTS OF PHASE EQUILIBRIA NEEDED BUT INADEQUATELY EXPLORED (21)

No - 63

Yes - 51

Example Given: Solid Solution Below One Percent (15)

Other Aspects:

- Explore Systems as a Function of P_{O_2} (6)
- Kinetics of Attainment of Equilibrium (5)
- Vapor Pressure (5)
- Immiscibility (Liquid and Solid) (3)
- Application of Phase Diagrams to Metastable or Non-Equilibrium Systems (2)

Table 36. ASPECTS OF PHASE EQUILIBRIA NEEDED BUT INADEQUATELY EXPLORED (21)

Experimental Methods for Obtaining Such Data

- Transmission Electron Microscopy
- Electron Diffraction (High Resolution Lattice Images)
- Vapor Pressure Measurements Across S.S. Region
- High Temperature X-Ray Diffraction in Mixed Gases
- Resistivity vs Temperature
- Scanning Electron Microscope
- Etch Techniques
- Neutron Diffraction
- IR Spectroscopy
- Neutron Activation Analyses

4.0 Discussion of Selected Conclusions

Several important points are worth discussion as a result of the analyses of the answers received from this questionnaire. With regard to needed experimental data, there are two areas of experimental research which are apparently badly needed. The first involves the study of various elements and oxides capable of oxidation/reduction under conditions of variable P_{O_2}. There is very little such data available for compilation. Only the simplest systems have so far been studied. The second area needed involves mixed systems containing refractories with slag or melt plus metal. Such mixed ternary or more complex systems are not primarily the classical concern of either ceramists or metallurgists. Consequently very few "academic" studies of such nature have been published. Probably a large amount of such data has been accumulated by individual industrial laboratories. Such data is generally considered proprietary and is very seldom published.

Regarding the compilation itself, there were several justified complaints which are worth reemphasizing. The first problem mentioned was that the time lag was too great between publication of the data and publication of the compilation. Attempting to supply a commentary for each diagram only increased the time lag. In answer to this criticism, the present technique utilizing guest editors for the commentaries has been established. It is obvious that 12 editors can produce more commentaries than one or two in the same amount of time. It remains to be proven that the system will work, but the coordinating editors presently hope to publish a new up-to-date supplement every three years with the next due in 1978.

The second comment is that the total coverage is not adequate. No matter how the editors try to find all published diagrams they are bound to miss some which were published in obscure journals or reports. Individuals have always been encouraged to submit references which they find have been missed, but this has never amounted to a large percentage. It is proposed that an advertisement for the publications be published several times a year in the trade journal(s) requesting readers to submit missed references from any date preceding some fixed value. Hopefully this will increase the probability of obtaining responses from the large community of users.

Another problem which will eventually have to be faced by the editors involves commentaries for the diagrams published in the 1964 and 1969 editions. It seems most likely that only the more important systems would require commentaries. The decision as to which diagrams should be republished with commentaries will have to be faced in the near future.

5.0 Summary of Conclusions

1) "Phase Diagrams for Ceramists" is providing an important service and should definitely be continued. The 186 respondents were overwhelmingly favorable. These responses were: very valuable - 162 (88%), moderately valuable - 20 (11%), and marginal value - 1 (1%).

2) Users classified themselves primarily as scientists (68%) but also substantially as engineers (38%); note that some classified themselves as both.

3) The largest percentage of respondents were in industry (44%). These industries included substantial representation from eight of the standard industrial categories plus 35 users in other categories. It is especially noteworthy that the user group extended far beyond the producers of ceramics and the users of ceramics in high temperature materials processing. Additional industrial categories cannot be briefly summarized but included those concerned with mining, chemicals, aerospace, and instruments.

4) A large group of users (20%) is in educational services. Many students in ceramics are taught from "Phase Diagrams for Ceramists" and use it as a personal reference book throughout their career.

5) Categorical uses by the 186 respondents are: sintering (64%), search for new compounds (51%), glass processing (34%), education (3.%), electronic materials (29%), crystal growing (28%), metal coating or processing (22%), smelting and refining (21%), geology (18%), energy conversion (17%), optical materials (16%), magnetic materials (16%), building materials (13%), environmental effects (9%), nuclear materials (15%), and other (10%).

6) Specific applications listed by respondents totalled 127. These cannot be briefly summarized but indicated great concern with high temperature corrosion mechanisms and limiting conditions of service in general as well as concern with advances in processing.

7) The present range of coverage of "Phase Diagrams for Ceramists" was approved by 68% of the respondents. The listings of specific systems of interest gives no indication that classical areas such as silicates are "mined out."

8) The range of coverage was indicated to be inadequate for their interests by 20% of the respondents. To satisfy their needs would require experimental or theoretical study rather than just compilation in most cases. Ninety respondents identified specific systems for which diagrams are needed and not available.

9) Some classes of systems for which high interest was indicated are not included in the compilation such as carbides and borides. There are no plans for coverage of these systems in the compilation at its present level of activity.

10) An important criticism is that the time lag is too great between the publication of the data and the publication of the compilation. It remains to be seen how much the new system of coordinating editors will reduce this time lag.

11) Respondents overwhelmingly favored continuing the commentaries which accompanied the diagrams in the 1975 Supplement. Some respondents called for additional types of information in the commentary which cannot be provided at the present level of activity.

12) Various areas of additional types of needed work (as opposed to specific systems) were suggested. Two are apparently badly needed. The first is the study of variable composition and structure in systems capable of oxidation or reduction. The second is the area of mixed oxide-metal systems typified by refractories in contact with slag or melt plus metal.

APPENDIX 1

QUESTIONNAIRE
on
"PHASE DIAGRAMS FOR CERAMISTS"
for use in a survey by the
American Ceramic Society

I. Description of Respondent.

1. Type of Training: 127☐ Scientist
71☐ Engineer
4☐ Other [please specify] ______

2. Highest Degree:
31 ☐ BS or BA [please specify field] ______
30 ☐ MS or MA [please specify field] ______
115 ☐ PhD or ScD [please specify field] ______
10 ☐ Other [please specify] ______

3. Present type of work [check as many as appropriate]:
143 ☐ research
85 ☐ development
18 ☐ production
40 ☐ technical management
46 ☐ education
9 ☐ other [please specify] ______

4. a] Are you a Member of the American Ceramic Society? 155☐ Yes
28☐ No

b] If you are a Member, to which Division(s) do you belong?
56☐ Basic Science
4☐ Cement
5☐ Ceramic-Metal Systems
21☐ Electronics
23☐ Glass
4☐ Materials & Equipment
5☐ Nuclear
29☐ Refractories
1☐ Structural Clay Products
1☐ Whitewares
12☐ No Division

5. Please check one or more of the following Standard Industrial Categories which best describe your employer:

- 6 ☐ 10 Metal Mining
- - ☐ 11 Anthracite Mining
- 2 ☐ 12 Bituminous Mining
- 3 ☐ 13 Oil and Gas Extraction
- 19 ☐ 14 Nonmetallic Minerals, except Fuels
- 20 ☐ 28 Chemicals and Allied Products
- 4 ☐ 29 Petroleum and Coal Products
- 4 ☐ 30 Rubber and Miscellaneous Plastic Products
- 50 ☐ 32 Stone, Clay, and Glass Products
- 15 ☐ 33 Primary Metal Industries
- 13 ☐ 34 Fabricated Metal Products
- 2 ☐ 35 Machinery, except Electrical
- 26 ☐ 36 Electrical and Electronic Equipment
- 4 ☐ 37 Transportation Equipment
- 10 ☐ 38 Instruments and Related Products
- 6 ☐ 39 Miscellaneous Manufacturing Industries
- 4 ☐ 52 Building Materials and Garden Supplies
- 46 ☐ 82 Educational Services
- - ☐ 84 Museums, Botanical, Zoological Gardens
- 2 ☐ 91 Executive, Legislative, and General
- 3 ☐ 95 Environmental Quality and Housing
- 2 ☐ 97 National Security and International Affairs
- 35 ☐ Other [please describe in your own words] ______________

____

6. [Optional]

Name and address of present employer

150 ______________________________

____

____

7. [Optional]

Your name 174 ______________________________

Address ______________________________

____

Telephone No. ______________

II. Uses of Phase Equilibria Data and Principles.

8. Areas of application of phase equilibria in your organization [check as many as apply]:

- 57 ☐ Education
- 33 ☐ Geology
- 39 ☐ Smelting and Refining
- 31 ☐ Energy Conversion Devices [turbines, batteries, gasifiers, etc.]
- 15 ☐ Nuclear Materials
- 117 ☐ Sintering of Ceramics
- 41 ☐ Metal Coating and Other Metal Processing
- 51 ☐ Crystal Growing
- 63 ☐ Glass Processing
- 54 ☐ Electronic Materials or Devices
- 29 ☐ Optical Materials or Devices
- 29 ☐ Magnetic Materials or Devices
- 23 ☐ Building Materials [cement, etc.]
- 17 ☐ Environment Effects [leaching, etc.]
- 93 ☐ Search for new compounds with desirable properties
- 19 ☐ Other [please specify] ____________________

9. Please describe one or more specific applications briefly in a way that shows type of information needed and purpose for which used.

127

10. Which classes of systems are of interest to you? Please indicate by 3 = High interest; 2 = Moderate interest, 1 = Some interest, 0 = No interest.

Oxides

144 Metal oxides

77 Alkali oxides

35 Phosphates

107 Silicates

40 Rare earths

53 Alkaline earths

Halides

25 Fluorides

24 Chlorides

1 Bromides

1 Iodides

General

31 Carbonates

32 Sulfates, Sulfides

10 Arsenides, Phosphides

6 Selenides, Tellurides

18 Nitrates and Nitrites

32 Oxynitrides, Nitrides

34 Borates

43 Carbides, Borides

14 Aqueous systems at 1 atm

12 Hydrothermal systems

15 Other [please specify] ______

III. Evaluation of PHASE DIAGRAMS FOR CERAMISTS as a publication of the American Ceramic Society.

11. How valuable do you consider PHASE DIAGRAMS FOR CERAMISTS as a continuing publication series by the Society?

162 ☐ Very valuable; in top priority category among special publications [Note: The JOURNAL, BULLETIN, and CERAMIC ABSTRACTS are not special publications].

20 ☐ Moderately valuable.

1 ☐ Marginal value

-- ☐ No value, should be discontinued

12. Considering the 1975 Supplement together with the 1969 Supplement and the 1964 volume, does the range of systems treated span your range of interests?

126 ☐ Yes

38 ☐ No. If no, please describe what other systems should be covered.

______

______

13. Within the range of systems treated are there gaps in coverage or compilation which need attention:

93 ☐ No

67 ☐ Yes. If yes, please describe. ______________________

____

14. Are there features of the systems to which more attention should be given during experimental studies [such as solid solution below the one percent level[?

89 ☐ No

69 ☐ Yes. If yes, please describe. ______________________

1 Don't know ____

15. Is the information given in the diagrams presented in a useful format?

165 ☐ Yes

10 ☐ No. If no, please suggest possible improvement. __________

____

16. Is the information in the commentaries in the 1975 Supplement useful?

7 ☐ No

153 ☐ Yes. If yes, is the length 7 ☐ too long?

2 Don't know 129 ☐ about right?

9 ☐ too short?

17. Is it useful to have information in the commentary on the following [please use 3 = high value, 2 = moderate, 1 = marginal, 0 = no value]:

103 Purity of starting material

85 Description of method of data determination

88 Information on the accuracy of the work

61 References to earlier work.

18. What additional information, if any, would you suggest be included in the diagrams and/or the commentaries?

43 ____

____

____

____

IV. Important needs for experimental and/or theoretical work not now being done. [Compilers are usually also research workers and influence other workers. Your indication of the relative importance of certain research gaps might lead to filling some of these gaps.]

19. Are there specific systems for which diagrams are needed and not available?

44 ☐ No

90 ☐ Yes. If yes, please describe. ______________________________

____

20. Are there parts of existing diagrams for which more detailed data are needed or which you suspect of being in error?

68 ☐ No

42 ☐ Yes. If yes, please describe. ______________________________

____

21. Are there aspects of phase equilibria which are needed and generally inadequately explored in most studies? [For example, solid solution below one percent.]

63 ☐ No

51 ☐ Yes. If yes, please describe the problem and, if possible, suggest experimental methods for obtaining such data.

____

____

____

APPENDIX 2

SPECIFIC APPLICATIONS OF INFORMATION OBTAINED FROM PHASE DIAGRAMS FOR CERAMISTS (9)

INDUSTRIAL

1. K_3PO_4-KNO_3 mixture to provide melt for ion exchanging glass articles. CaF_2-NaF-SiO_2 system for studying crystalline nature of fluoride opacified glasses

2. What primary phase should we expect in a devitrification process and what are the optical properties of this phase?

4. Study of reasons for different melting (dissolution) rates of various alumina sources in glass batch. High melting points of K-feldspar (lepidolite-mica) and nepheline were considered important possibilities.

6. Slagging reactions - influence of all industrial slags on refractory oxides, on liquid formation
e.g. - Which refractory oxides are most stable (least influenced) by attack of: V_2O_5, F, Borosilicates?

7. Phosphate bonding applied foundry sand technology requires that we achieve strong room temperature strengths, the strengths to be retained as the bonded sand is shock heated and for the sand to fuse (intergrain liquids) minimally. The low fusion is needed to assure easy knockout or removal from cores or inside geometries of castings. Steel castings, being the highest temperature metals, are most demanding of sands and binders.

11. 1) Liquidus in multicomponent systems for glaze development and glass seal research 2) Primary phase fields in refractory development, e.g. - cordierite refractories.

12. In the manufacture and development of cordierite refractory compositions, we use the MgO-Al_2O_3-SiO_2 diagram extensively and with great success.

13. 1) Determination of amount of liquid formed when basic refractories are fired to various temperatures in the presence of various metallurgical slags, molten metals, various sorts of atmospheres, etc. 2) As a guide to suggest amounts of dolomite to be added to achieve desirable properties (fluidity, minimum corrosive attack on refractories) on refractories in blast furnaces, basic oxygen and electric arc steelmaking furnaces. 3) If phase equilibria data were available in sufficient detail we should use them in development of zircon, zircon-alumina, zircon-mullite and zircon-magnesia refractories.

21. Solubilities of Ni and Fe in some silicate glasses; phase relations gave maximum % soluble prior to crystallization.

22. Compositions where one component is alumina or silicon carbide; suitable for abrasives.

23. Much of my work involves phase identification. When working with known systems, I find the diagrams very useful for determining likely phases to be encountered.

26. Phase information for glasses used to produce cermet resistors, etc. for electronic applications. Source of references for literature search.

29. High MgO basic refractories used as checker brick in glass regenerators undergoes alteration due to high temperatures and furnace carryover. Long term cyclic conditions are not always same as found in phase diagrams. Many phase diagrams published are apparently not quite equilibrium diagrams, either. A researcher who needs to recommend a material for such an application may get misleading results from phase diagrams. Thus information needed is long term equilibrium - kinetics are important. More specific applications of great concern are of proprietary nature and unfortunately cannot be discussed here.

30. The effect of steel or slag components, such as MnO, K_2O, on refractories is predicted using phase equilibria data. It is used primarily in the iron and steelmaking furnaces.

37. I used metal-metal systems quite frequently for brazing studies and reactivity with other metals. With the heavy activity in metallizing plating, and brazing ceramics the diagrams published by the American Society for Metals is of great help.

NOTE: In a compilation of "Phase Diagrams for Ceramists" I feel the aqueous systems could be omitted.

39. Melting points and eutectic formation in systems $BeO-SiO_2$, $BeO-SiO_2-MgO$, $CaO-SiO_2$, $B_2O_3-SiO_2$, $Al_2O_3-B_2O_3-SiO_2$, $Li_2O-Al_2O_3-SiO_2$, WO_x-SiO_2, $B_2O_3-WO_x-SiO_2$ and other systems. The information is needed to predict the behavior of silicon carbide and silicon nitride ceramics (containing these additions or impurities) in oxidizing environment at high temperatures.

41. In the glass industry, if there is refractory corrosion of the arch, what might be possible causes?

42. Seeking new high temperature compounds, or limitations of current materials.

44. At present most of my needs are in systems involved with crystal growth. One such system is the system $Cs_2O-As_2O_5-H_2O$ (or D_2O). I realize this is not a "ceramic" system, but you are way beyond this point now. However, checking discloses not only not the 3-component diagram, but even one of the two-component boundaries is missing - $Cs_2O-As_2O_5$. I have in my possession two gov't reports, circa 1969, and one circa 1974 with incomplete information. I realize it is unreasonable to expect all work to be already done. But this is how I start. We then go on from there.

46. Large area ceramic semiconductors (polycrystalline) for use in optoelectronics. (A) Traveling zone melting for removal of voids and reduction in width and number of grain boundaries. (B) Controlled directional cooling. (C) Effects of annealing.

48. Preparation of semiconducting barium titanates and microwave titanate required information on phase stabilities and homogeneity ranges. Up-to-date information such as #4302 was very valuable.

49. What are the reaction products of magnesia with cordierite, how can this be used in an auto exhaust catalyst system?

51. Glass-liquidus studies and tests are performed by our laboratory. As are refractory compositional studies. We use the phase diagram information daily and would like to see this information updated every 3-5 years.

Also there are many low temperature reactions and phase relationships that are not given in the current publications, i.e., 300°C to 1000°C - these would be useful.

186. 1) Need TTT diagrams of common alloys 2) Need nucleation and crystallization rates of glasses 3) Need fundamental properties of glass vs composition (i.e. refractive index, absorption, density) 4) Oxidation rates of alloy with temperature.

58. To explain refractory failure such as liquidus situations in soaking pits, etc.

59. Slag composition for tin melting, i.e. concentrates to metallic tin. Oxide reduction to metallic state - tin and other metals.

60. We are generally very interested in the effects of lithium compounds and minerals on the properties of ceramic compositions (Corning Ware, etc.)

63. Sintered thermistor flake was behaving erratically. Analysis of components, microstructures and phase diagrams yielded firing information, allowing recommendations to vendor to amend process.

69. Phases and compounds formed as a result of sintering a mixture of oxides.

70. Establishing liquidus and optimum high temperature stability of ceramic phases as related to ceramic cores, casting shells, etc.

73. Information given in the previous publications is sufficient to our purposes. We use these diagrams to formulate brazing fluxes, refining slags, etc.

75. Refractory attack occurred at bottom of furnace when metal temperature was lowered 50°C. Analysis of phase diagram showed that 50°C drop lowered bottom of furnace operating temperature below melting point of anorthite which built up during low end of temperature cycle. Upon heating to upper end of metal melting temperature, corrosive liquid was formed which ate the SiO_2 lining of the induction furnace. Bottom end of temperature range was raised 50°C and problem was eliminated. Subsequently we used a low calcium additive to metal which minimized overall attack.

76. Literature survey

77. - Heat exchangers in high temperature turbines
    - Catalyst supports
    - Cement and concrete additives

78. β-Alumina: - influence of various additives or impurities on phase composition
    Silica-nitride: - influence of impurities on phases present on surface of grains.

79. 1) Very low temperature sealing glasses (not water soluble nitrates) e.g. binary and ternary diagrams needed on low melting oxides, for solder glasses 2) Information on electrical conductivity in some systems (e.g. V_2O_5 systems) for resistive films 3) Information on glass forming regions in binary, ternary, etc. systems. Aid in glass melting 4) Information on missing binary and ternary systems for general reference.

86. Degree of refractoriness of system. Possible reactions of materials in contact. Solid solutions.

92. To find liquidus temperatures of glass systems of current or potential interest.

96. Possible reaction that products will encounter such as $CaO-SiO_2-Al_2O_3$ vs S on V_2O_5- on Na_2SO_4- on NaCl.

99. The melting temperature of compounds allow selection of materials that are compatible with electronic device processing and packaging, i.e. glass on integrated circuits or glass ceramic coatings on ceramic thick film electrical circuit assemblies.

104. Slag chemistry as related to pyrometallurgical processes.

105. Calculating supersaturations for crystal growth. Crystal growth temperatures.

107. Compound and liquid formation during liquid phase sintering in multi-component oxide systems.

109. Diagrams involving alkali sulfates and calcium sulfate, e.g., K_2SO_4-$CaSO_4$, have been useful in identifying and studying compounds occurring in some portland cement clinkers and in cement kiln dusts.

121. Need information on solubility versus composition of Ta_2O_5 and WO_3 and other oxides for use as dielectric oxide.

123. Primarily use is to ascertain possible compositional shifts in production glasses where the primary crystal phase has been found to change. Specific ternaries are often used to aid interpretation in new glass development.

124. Estimate stable glass-forming regions in unexplored systems by comparison with somewhat similar systems.

126. Optimize oxide ratios to minimize phase separations, find less expensive oxide fluxes, find reactions to expect of oxide-metal at high temperature.

131. In developing new, high temperature oxide ceramics it is necessary to know the eutectic temperatures in the systems of interest to determine their theoretical use temperature.

133. In formulating glass frits, it is important to determine areas of potential phase separation. Examination of the appropriate phase diagrams gives a clue as to what may be expected.

137. For example, in synthesizing and modifying and doping of magnetic materials, phase equilibria data are used to (1) estimate the temperature required for synthesis in a particular system, (2) get an idea of the extent of solid solution tolerated in a particular system, (3) help identify potential impurities (compounds adjacent to the desired phase in the phase diagram), (4) identify other similar phases in related systems.

147. Used to determine amount of mullite that could theoretically exist in a mixture of clays, feldspars and refractories, and at what temperature the mullite could form.

153. "Phase Diagrams for Ceramists" is used primarily when initiating studies in unfamiliar systems. Determinations of material compatibilities (including non-reactive setter materials) melting and calcining temperatures and expected phase formations are required. In the analytical area, it is useful in combination with other data such as x-ray diffraction for phase identification.

155. Compounding 2 or more ceramic materials and sintering.

159. Formulation and application of low temperature solder glasses for the semiconductor industry. U.V. transmitting window for electronic devices.

158. Classified

160. I have probably used diagrams to find thermal stability ranges of compounds more than anything else. Diagrams are useful in interpeting complicated x-ray diffraction patterns in ceramic materials.

163. Ash- ceramic behavior prediction in gasifiers. Ash behavior in various thermal and gaseous environments.

Slag- steel melt interactions

Oxidation- sulfidation problems in turbines

Chemistry in molten carbonate baths. Also interaction of molten carbonates with ceramics.

168. 1) Iron/steel refining processes: mineral composition of slags; variation w/temperature; viscosity; reactivity to brick composition. 2) Grain/brick production: sinterability as related to: a) s.s. induced defect structures; b) liquid phases present - viscosity, composition, transport tubes. 3) "Binders" i.e. deliberate low-temp melt phases - examination of melt composition variation with increasing temp - retrograde solubility if any, properties of melts in systems Na_2O-K_2O-B_2O_3-SiO_2-CaO-MgO.

169. Proprietary

171. Geological phase information has been useful to me (notice that Geology is checked above) not only because rocks and minerals concern me as raw materials for ceramics and glasses; but also because I use rocks and minerals - as well as ceramics and other synthetics - for the purpose of exploring and testing microscopic methods.

175. Designing new coating systems via powder processing and flame spraying to achieve enhanced wear resistance and related properties.

181. Regions of glass formation - new and modified glass - refractory reactions

184. To investigate extent of solid solution regions of selected compounds in an attempt to alter the properties of that compound.

8. Crystal growth in silicates and oxides from melt. High temperature solvent for crystal growing the above compounds.

9. As a petrologist, I am concerned with systems involving the formation of igneous and metamorphic rocks - as well as high pressure studies dealing with materials found in the earth's mantle.

   Your volumes were very useful to me when writing a book entitled "The Interpretation of Geological Phase Diagrams".

14. Essential for determining possible areas of glass formation.

25. Used ZnO - P_2O_5 diagram to find reference to $Zn_2P_2O_7$ research.

33. I have been interested in precipitation in ceramics. Knowledge of the phase diagrams tells one whether precipitation will occur or not.

35. Calculations of coherent metastable phase equilibria from incoherent equilibrium solvi data of cubic binary oxides, i.e., CaO-MgO, CaO-NiO, CoO-NiO, MgO-$MgAl_2O_4$. Estimation of composition limits of metastable glasses, i.e., Al_2O_3-SiO_2 for annealing experiments. Accurate liquidus determinations for quenching experiments.

40. We are performing research on welding slags and fluxes.

    NOTE: These books are valuable! They need to be continued with the increasing amount of new phase stability and equilibrium information being generated.

47. Use these to decide time-temperature schedules for heating ceramics to study phase transformations.

52. 1) Will we melt the bottom out of our furnace? Al_2O_3 lining BeO ceramic - check lowest melting compound. 2) Sintering refractory castables - and Al_2O_3-SiO_2-CaO phase diagram for liquidus, solidus, phases formed.

57. MHD Slag Thermochemistry - need T, X_i, P_{O_2}, existence data for increasingly complex systems.

    Solid State Reactions - need phase relations to decide firing conditions.

61. 1) Fluxes for crystal growth, multicomponent systems needed.
    2) Effect of impurities in ceramic compositions of predominately one phase - multicomponent systems needed.
    3) Oxygen stoichiometry for oxides.

65. In crystallization from the melt, in a non-congruently melting system, the diagrams are used to identify crystal products and their approach to equilibrium.

67. Research

83. In studying sintering, phase diagrams are extremely useful in predicting whether impurities or additives will form a liquid or promote a defect structure.

88. Most of the applications involve specific problems related to some consulting or trouble-shooting assignment. The educational uses are (have been) related to exposure of non-ceramists to ceramic phase equilibria, including tracing crystallization paths from the liquidus, equilibrium phases present, and interpretations of non-equilibrium observations.

91. 1) Melting temperature of a proposed complex castable ceramic in the $MgO:Al_2O_3:CaO:P_2O_5$ system. 2) Region of immiscible and spinodal separation in the $PbO-B_2O_3-Al_2O_3$ system. 3) Effect of oxygen pressure on the shear structure of Nb_2O_5 - suboxide. 4) YF_3-Y system and similar systems.

98. The system $MgO-FeO-Fe_2O_3-CaAl_2Si_2O_8-SiO_2$ has been studied at several different oxygen fugacities at 1 atm total pressure, and now is being investigated at 10,000 atm total pressure. This serves as a model for the more complex natural magmas, e.g., basalts and andesites, providing an estimate of the path of crystallization as a function of oxygen fugacity and pressure. This in turn is needed to explain the origin of the diverse, but related compositions of magmas being extruded at the surface of the earth.

102. What salt mixtures have low eutectic temperatures for strengthening glass?

108. Phase chemistry for electrodes/insulators in coal-fired MHD available in phase diagrams.

113. Compatibility of materials and crucibles. Liquid compositions which precipitate desired crystal products. Melting temperatures and behavior.

120. Corrosion of refractories - with equilibrium diagrams it is possible to at least get an order of magnitude judgement of instability of a refractory-slag combination.

129. Use in choosing systems for study as model systems for steelmaking slags. Primarily interested in choosing silicate systems with relatively large fields above low liquidus curves.

136. Prediction of high-temperature reactions in metal-oxide systems.

142. The use of phase diagrams to determine phases present at a certain temperature, pressure and composition. Prediction of stable phases and compounds. Research involving the slight change in the composition of a semiconductor oxide to modify its electronic and energy absorbing properties.

146. Detailed knowledge of the systems $CaO-SiO_2-Al_2O_3-MgO-Fe_2O_3$ (FeO) P_2O_5-MnO.

In behalf of a study on blast furnace slag (granulated)

182. - solid-state reactions of powders
- solubility of additives
- composition and temperature of eutectics
- effects of contamination in furnaces

71. We need information on glass forming areas in the phase diagrams.

116. Refractories: research, application

165. Phase transformations in actinide oxide systems, relevant for the development of new ceramic fabrication procedures in the nuclear area, are obtained frequently from your publications.

82. I was interested in what might crystallize out from lignite flyash upon roasting. This is in the system $CaO-Al_2O_3-SiO_2$ as a final approximation. From the chemical analysis the equilibrium firing product should be anorthite. It was in fact, though it takes some time to nucleate and crystallize. The diagram correctly predicted this result (which was unfavorable for our human desires).

140. 1) thermodynamic properties of metallurgical slags
2) devitrification of glasses
3) synthesis of minerals

100. Crystal growing... research work is being conducted to develop a new method for crystal growth using fused salts electrolysis which includes smelting techniques. Electronic material...new compounds are being searched by applying phase equilibria of tri- or tetra-components.

138. Melting and determination of a new glass forming system.

150. Materials for solar energy conversion

173. Doping effects improving materials properties. Melting temperature drops and reactions among 2 or 3 materials contacted. Compound formations among 2 or 3 components.

172. One application consists of designing a suitable slag for a smelting process based on the gangue material of the ore. Use is made of the phase diagrams to determine what flux would be used to make a slag having a suitable liquidus temperature.

148. 1) Illustrative phase diagrams for a short course I teach on "Understanding Phase Diagrams". 2) Checking for compound formation, solid solution, phase transitions, etc. among oxide systems relevant to my research in ceramic nuclear waste forms, catalysis, phosphors, etc.

164. In teaching about the iron blast furnace. Slag composition is selected based on SiO_2/Al_2O_3 ratio of charge to which CaO, MgO is added. Ceramic properties (a) to get acceptable melting point, (b) low viscosity, (c) chemical behavior for impurity control, (1) activity of SiO_2, (2) sulfur capacity.

174. 1) Teaching students how to use phase diagrams. 2) Use petrological diagrams to help interpret field and microscope information on the formation of igneous and metamorphic rocks.

183. Educational - all types of diagrams, as complete as possible. Research - glass melting, crystallization (metastable phases would help).

Refractory selection (gas diagrams would help).

NOTE: Commentary in new supplement is very useful.

GOVERNMENT AND NATIONAL LABORATORIES

28. Phase equilibria for interpreting geochemical systems.

66. Inorganic chemical reactions and finding suitable containment for performing at $\geq$1000°C.

80. 1) Synthesis and sintering of spinels for coating Mo. 2) Eutectic temperatures of chloride compositions resulting from chlorination of minerals. 3) $Li_2O:MgO:Al_2O_3$, solidus, liquidus and glass formation? 4) Solid solutions, chromates, ZrO_2, etc. for heating elements.

125. Flux growth of two and three component oxide systems. Need to know compound melting points, solid plus liquid regions, final freezing points: Example: Growth of $KTaO_3$ from a K_2CO_3 rich melt.
Growth of oxide from fluoride/chloride flux melts.

UNIDENTIFIED

3. Glass melting reactions

Refractory reactions at high temperatures: a) in contact with glass, b) in melter atmosphere, c) in waste gas system

Glass devitrification

55. In determining proper refractory and anticipating wear mechanism where the process is new or uncommon. Relative viscosity of liquid phases would be important additional information.

85. Possible crystal probe that may precipitate out from a complex glass system(s) in order to upgrade both physical and chemical properties.

128. Formation of barium zirconate. Formation of calcium stannate.

157. Perhaps the following is adequate: (from R. N. Rhines, Phase Diagrams in Metallurgy, 1956 Preface) (replace ceramics for metallurgy and ceramist for metallurgist)

> "Phase diagrams mean more to the metallurgist (ceramist) than mere graphical records of the physical states of matter. They provide a medium of expression and thought that simplifies and makes intelligible the otherwise bewildering pattern of change that takes place as elemental substances are mixed one with another and are heated or cooled, compressed or expanded. They illumine relationships that assist us in our endeavor to exercise control over the behavior of matter. These are no accidental by-products of a system devised primarily for the recording of physical data. They exist because the basic features of construction of all phase diagrams are dictated by a single natural law, the phase rule of J. Willard Gibbs, which relates the physical state of a mixture with the number of substances of which it is composed and with the environmental conditions imposed upon it.
>
> Gibbs first announced the phase rule in 1876, but it was not until the opening of the present century that its significance was appreciated by any substantial fraction of the scientific world. To Bakhuis Roozeboom is due much of the credit for interpreting the phase rule to the scientific public and for demonstrating its usefulness in meaningful..."

170. Determine liquidus temperatures for glass batches; locate eutectics in search for probable glass-formers; find refractive index of glass compositions.

176. A recent application involves glass-metal and cermet seals and methods of bonding parts together. Interface conditions are of critical concern. Temperature information most helpful.

FOREIGN

151. Oxidation products, compatibility metals - ceramics.

144. Studies on degradation of refractories in aggressive atmospheres. (Magnesite-refractories in alkali-sulfate containing gases) Compound formation in the mullite-corundum area.

89. a) Prediction of the likely extent of attack by an iron and steel making slag on a particular refractory composition. b) Investigation of the possible effects of small amounts of oxide addition to a particular refractory oxide on sintering characteristics. c) Examination of the changes in phase assemblage taking place in a refractory concrete on heating.

93. Determining the number of phases present in metallurgical slag during refining.

97. 1) 1466 KF-ZrF_4 system, useful in studies on the production of K_2ZrF_6. Phase diagram showed that at reaction temps K_2ZrF_6 disproportionates. Also shows existence of K_3ZrF_2 eutectic, very important in reaction mechanisms. 2) 362: ZrO_2-SiO_2 - useful showing solid solution of SiO_2 in ZrO_2. 3) 361 in same way as 362.

156. Estimation of liquidus temperatures of more complex systems. Estimation of primary phases likely to crystallize during test treatments.

145. Calculating liquid contents of, for example, fireclay refractories at various temperatures.

178. Assessment of potential virtues or deficiencies of newly developed alumino-silicates or basic refractories.

Mechanism of failure of refractories in contact with metallurgical or glass-making slags.

127. 1) Calculation of change in liquid content with composition in appropriate 2 and 3 component systems in order to predict possible thickness of liquid film found by reaction of surface SiO_2 on silicon nitride grains with added mineralizers and with impurities. Appropriate diagrams needed: MgO-SiO_2, MgO-Li_2O, MgO-CaO-SiO_2, etc.

2) Calculation of overall chemical compositions to give desired phase assemblages in experimental basic refractory materials at chosen temperatures.

87. Study of refractories corrosion by glasses; price of appropriate refractories for regenerators. Study of glass-component reactions.

112. Eutectic compositions for ds composites. Reactions in sintered composites.

154. Substitute structure of mullite by others - e.g. anorthite-gehlenite + quartz in e.g. fast-fired tiles. To find cheap (new) sources of not only minerals but mainly rock - use of slag in this connection. To find out additives like Li-compounds to make such process manageable. Economics of heat treatment of raw material compounds.

167. - liquidus phase of materials refractories
- sintering
- cements phase

NBS-114A (REV. 7-73)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET**	1. PUBLICATION OR REPORT NO. NBS SP 486	2. Gov't Accession No.	3. Recipient's Accession No.

4. TITLE AND SUBTITLE	5. Publication Date
USER EVALUATION OF "PHASE DIAGRAMS FOR CERAMISTS" AND IMPLICATIONS FOR RELATED DATA AND RESEARCH PROGRAMS	August 1977
	6. Performing Organization Code

7. AUTHOR(S)	8. Performing Organ. Report No.
R.S. Roth, L.P. Cook, T. Negas, G.W. Cleek and J.B. Wachtman, Jr.	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. Project/Task/Work Unit No.
NATIONAL BUREAU OF STANDARDS DEPARTMENT OF COMMERCE WASHINGTON, D.C. 20234	11. Contract/Grant No.

12. Sponsoring Organization Name and Complete Address *(Street, City, State, ZIP)*	13. Type of Report & Period Covered
Same as Item 9	14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

Library of Congress Catalog Card Number: 77-10496

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

A survey was made of the needs of the users of "Phase Diagrams for Ceramists," a continuing special publication series published by the American Ceramic Society under the general editorship of the National Bureau of Standards. The results overwhelmingly support continuation of the series, but point to needs for expanded coverage, fuller commentaries, and reduced publication time. The results also identify needs for greater effort on specific types of experimental and theoretical phase equilibria studies including the effects of variable oxygen pressure and complex metal-ceramic systems.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

American Ceramic Society; ceramics; phase diagrams; "Phase Diagrams for Ceramists"; phase equilibria; user evaluation

18. AVAILABILITY [X] Unlimited	19. SECURITY CLASS (THIS REPORT)	21. NO. OF PAGES
[ ] For Official Distribution. Do Not Release to NTIS	UNCLASSIFIED	70
[X] Order From Sup. of Doc., U.S. Government Printing Office Washington, D.C. 20402, SD Cat. No. C13.10:486	20. SECURITY CLASS (THIS PAGE)	22. Price $2.10
[ ] Order From National Technical Information Service (NTIS) Springfield, Virginia 22151	UNCLASSIFIED	

USCOMM-DC 29042-P74

NBS TECHNICAL PUBLICATIONS

PERIODICALS

JOURNAL OF RESEARCH reports National Bureau of Standards research and development in physics, mathematics, and chemistry. It is published in two sections, available separately:

• **Physics and Chemistry (Section A)**

Papers of interest primarily to scientists working in these fields. This section covers a broad range of physical and chemical research, with major emphasis on standards of physical measurement, fundamental constants, and properties of matter. Issued six times a year. Annual subscription: Domestic, $17.00; Foreign, $21.25.

• **Mathematical Sciences (Section B)**

Studies and compilations designed mainly for the mathematician and theoretical physicist. Topics in mathematical statistics, theory of experiment design, numerical analysis, theoretical physics and chemistry, logical design and programming of computers and computer systems. Short numerical tables. Issued quarterly. Annual subscription: Domestic, $9.00; Foreign, $11.25.

To begin publication as a single journal, July-August 1977

DIMENSIONS/NBS (formerly Technical News Bulletin)—This monthly magazine is published to inform scientists, engineers, businessmen, industry, teachers, students, and consumers of the latest advances in science and technology, with primary emphasis on the work at NBS. The magazine highlights and reviews such issues as energy research, fire protection, building technology, metric conversion, pollution abatement, health and safety, and consumer product performance. In addition, it reports the results of Bureau programs in measurement standards and techniques, properties of matter and materials, engineering standards and services, instrumentation, and automatic data processing.

Annual subscription: Domestic, $12.50; Foreign, $15.65.

NONPERIODICALS

Monographs—Major contributions to the technical literature on various subjects related to the Bureau's scientific and technical activities.

Handbooks—Recommended codes of engineering and industrial practice (including safety codes) developed in cooperation with interested industries, professional organizations, and regulatory bodies.

Special Publications—Include proceedings of conferences sponsored by NBS, NBS annual reports, and other special publications appropriate to this grouping such as wall charts, pocket cards, and bibliographies.

Applied Mathematics Series—Mathematical tables, manuals, and studies of special interest to physicists, engineers, chemists, biologists, mathematicians, computer programmers, and others engaged in scientific and technical work.

National Standard Reference Data Series—Provides quantitative data on the physical and chemical properties of materials, compiled from the world's literature and critically evaluated. Developed under a world-wide program coordinated by NBS. Program under authority of National Standard Data Act (Public Law 90-396).

NOTE: At present the principal publication outlet for these data is the Journal of Physical and Chemical Reference Data (JPCRD) published quarterly for NBS by the American Chemical Society (ACS) and the American Institute of Physics (AIP). Subscriptions, reprints, and supplements available from ACS, 1155 Sixteenth St. N.W., Wash. D. C. 20056.

Building Science Series—Disseminates technical information developed at the Bureau on building materials, components, systems, and whole structures. The series presents research results, test methods, and performance criteria related to the structural and environmental functions and the durability and safety characteristics of building elements and systems.

Technical Notes—Studies or reports which are complete in themselves but restrictive in their treatment of a subject. Analogous to monographs but not so comprehensive in scope or definitive in treatment of the subject area. Often serve as a vehicle for final reports of work performed at NBS under the sponsorship of other government agencies.

Voluntary Product Standards—Developed under procedures published by the Department of Commerce in Part 10, Title 15, of the Code of Federal Regulations. The purpose of the standards is to establish nationally recognized requirements for products, and to provide all concerned interests with a basis for common understanding of the characteristics of the products. NBS administers this program as a supplement to the activities of the private sector standardizing organizations.

Consumer Information Series—Practical information, based on NBS research and experience, covering areas of interest to the consumer. Easily understandable language and illustrations provide useful background knowledge for shopping in today's technological marketplace.

Order **above** *NBS publications from: Superintendent of Documents, Government Printing Office, Washington, D.C. 20402.*

Order **following** *NBS publications—NBSIR's and FIPS from the National Technical Information Services, Springfield, Va. 22161.*

Federal Information Processing Standards Publications (FIPS PUBS)—Publications in this series collectively constitute the Federal Information Processing Standards Register. Register serves as the official source of information in the Federal Government regarding standards issued by NBS pursuant to the Federal Property and Administrative Services Act of 1949 as amended, Public Law 89-306 (79 Stat. 1127), and as implemented by Executive Order 11717 (38 FR 12315, dated May 11, 1973) and Part 6 of Title 15 CFR (Code of Federal Regulations).

NBS Interagency Reports (NBSIR)—A special series of interim or final reports on work performed by NBS for outside sponsors (both government and non-government). In general, initial distribution is handled by the sponsor; public distribution is by the National Technical Information Services (Springfield, Va. 22161) in paper copy or microfiche form.

BIBLIOGRAPHIC SUBSCRIPTION SERVICES

The following current-awareness and literature-survey bibliographies are issued periodically by the Bureau:

Cryogenic Data Center Current Awareness Service. A literature survey issued biweekly. Annual subscription: Domestic, $25.00; Foreign, $30.00.

Liquified Natural Gas. A literature survey issued quarterly. Annual subscription: $20.00.

Superconducting Devices and Materials. A literature survey issued quarterly. Annual subscription: $30.00. Send subscription orders and remittances for the preceding bibliographic services to National Bureau of Standards, Cryogenic Data Center (275.02) Boulder, Colorado 80302.