PHASE DIAGRAMS FOR CERAMISTS
VOLUME VII

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The Phase Diagrams published in this volume were collected and reviewed by the Phase Diagrams for Ceramists Data Center, located in the Institute for Materials Science and Engineering of the National Institute of Standards and Technology. Significant support from the American Ceramic Society was crucial in providing this important reference information to the ceramics community.

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Preface

This volume is the seventh in the series *Phase Diagrams for Ceramists* and the second to appear since the National Institute of Standards and Technology (NIST) [formerly National Bureau of Standards] and the American Ceramic Society (ACerS) embarked on a jointly-sponsored Ceramic Phase Equilibria Program. The goal of the Program is to support growth and progress in the ceramics industry by providing relevant critically-evaluated phase diagrams. To achieve this, a multiyear program was established to improve currency with the archival literature and to provide critically-evaluated phase diagrams for oxides, salts, carbides, nitrides, borides, compound semiconductors, and chalcogenides. Computer graphics, database management, computer evaluation and predictive modeling are being used where possible to produce databases for distribution and generation of computer-typeset products. Program updates appear periodically in the American Ceramic Society Bulletin.

Program Origins: For over fifty years the National Bureau of Standards (now NIST) and ACerS have collaborated on the publication of evaluated phase diagrams of ceramic systems, best represented by the series *Phase Diagrams for Ceramists*, Volumes I-V. The joint Ceramic Phase Equilibria Program, representing a continuation and expansion of the effort to make ceramic phase information readily and comprehensively available, was initiated in December 1982.

Program Responsibility: To achieve the goals of the expanded program a multiyear effort was established with support from NIST and other federal agency programs and from a fund-raising effort managed by the ACerS. NIST provides overall coordination and technical guidance and ensures quality data coverage and evaluation. NIST has also developed a prototype PC graphics database. The ACerS is responsible for the production aspects and dissemination of the data in both printed and computer database forms.

Sponsorship: The fund-raising effort managed by ACerS is an ongoing activity. As of June 1989 a total of $2,486,410 has been contributed or pledged to the program. There are five basic categories of participation in the Ceramic Phase Equilibria Program: Primary Sponsors, $200,000 or more; Sponsors, $100,000 or more; Affiliate Sponsors, $25,000 or more; Contributors, $5,000 or more; and Members and Friends, any smaller amount. Contributions to the program, through June 1989, from individuals and the following organizations are gratefully acknowledged.

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Introduction

I. GENERAL EDITORS' COMMENTS

This volume, VII, in the *Phase Diagrams for Ceramists* series includes 934 Figures containing 1057 diagrams of salt systems collected from the literature between 1975 and 1983,[1] together with some overflow from earlier volumes. Only systems with halide and certain oxyanion salts are included in the present volume. "Mixed" systems containing salts with other substances are not included here (except for selected salt-metal and salt-gas systems) and will be covered in future volumes. With the exception of certain salts with oxygen-containing anions, no oxides are included.

For purposes of system classification, the rule used in deciding whether a substance is a "salt" or an "oxide" is as follows. Compounds of elements whose oxides are solid at 25°C and 1 atm are designated as the component oxides and these were included in Volume VI (e.g., chromates, molybdates, tungstates, etc.). Oxyanions of those elements whose oxides are gaseous under the above conditions are classified as salts and are included in the present volume (e.g. carbonates, nitrates, sulfates, chlorates, etc.).

There are two significant differences between Volume VII and previous volumes: (1) the use of formatted commentaries and (2) the inclusion of a substantial number of thermodynamically optimized diagrams. Formatted commentaries have been introduced in an attempt to minimize phraseology while maintaining uniformity of coverage and allowing the reader to find the desired information quickly (e.g., X-ray confirmation of the solid solutions and compounds on the diagram, methods used in determining the liquidus, etc.). This volume is also the first to contain optimized diagrams, diagrams generated by the application of thermodynamic methods in producing the best fit to binary data from many sources. A number of the ternary diagrams included have been calculated from the optimized binary data. In this area, the General Editors gratefully acknowledge the competent efforts of Prof. Arthur D. Pelton, Dr. James M. Sangster, and their colleagues at the Facility for Analysis of Chemical Thermodynamics at the École Polytechnique de l'University de Montréal (see Section II of this Introduction).

There are individuals whose names do not appear on the title page who deserve acknowledgement and thanks for their contributions to the publication of this book. The graphics programs with which diagrams were digitized, edited, and plotted are those used for Volume VI, written by Peter K. Schenck with Jennifer R. Dennis Verkouteren. Cathy Senna and Teresa Brittle assisted in the keyboarding of commentary texts. Thanks also go to Mary A. Clevinger for advice and assistance in the handling of the typeset text material. The following people assisted in the phase diagram graphics data effort to produce Volume VII: Daniel Pennington, Raymond Yang, Timothy King, Richard Wilson, Peggy O'Neil, Steven Peart, Thomas Green, Theresa Messina, and Barbara Lee.

For a fuller discussion of the procedures used in collecting, evaluating, and editing the diagram information, and a description of the computer graphics software used in digitizing, storing, retrieving, and plotting the phase diagrams, the reader is referred to the "General Guidelines" and "Graphics Program" sections in Volume VI.

The individuals listed below are the editors who contributed to Volume VII. The commentaries submitted by each are identified in the book by the initials shown.

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[1] C. G. Messina, M. A. Clevinger, L. P. Cook, and R.S. Roth, *Phase Diagrams for Ceramists Bibliographic Update for Oxides and Salts through January 1, 1984*, 182 pp (The American Ceramic Society, Inc., Westerville, Ohio, January 1986).

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II. CRITICAL COUPLED EVALUATION OF PHASE DIAGRAMS AND THERMODYNAMIC PROPERTIES OF BINARY AND TERNARY ALKALI SALT SYSTEMS*

by James M. Sangster and Arthur D. Pelton†

1. *INTRODUCTION*

There exists a wealth of data on phase diagrams involving salts of the alkali metals in previous volumes of *Phase Diagrams for Ceramists*[1] and in other data compilations.[2-7] Where systematic critical evaluation has been attempted, the contribution of a thermodynamic simultaneous analysis of the data has not been fully utilized. For the common-ion binary systems of salts of the alkali metals, there exists also a large amount of data on mixing and excess thermodynamic properties[8] in both the liquid and solid states. A comprehensive coupled evaluation of the phase diagrams and thermodynamic properties of 124 binary and 60 ternary alkali salt systems is presented in this volume.

The binary systems include all 40 possible common-anion (AX-BX) and all 30 possible common-cation (AX-AY) systems involving the alkali halides (A, B = Li, Na, K, Rb, Cs; X, Y = F, Cl, Br, I), as well as all 54 additional possible common-cation and common-anion binary systems involving the cations Li^+, Na^+, K^+ and the anions F^-, Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-}, OH^-.

The ternary systems include all 60 possible common-anion (AX-BX-CX) and common-cation (AX-AY-AZ) systems involving the alkali halides.

An extensive literature survey of available phase diagram and thermodynamic data was carried out for all binary and ternary systems.

Binaries

A critical analysis and evaluation of the binary data was performed with a view to obtaining a "best" evaluated phase diagram and a set of "best" evaluated thermodynamic parameters for each system. To this end, a computer-assisted coupled analysis of the phase diagram data and the thermodynamic data for each system has been employed. Mathematical expressions for the thermodynamic properties of all known phases have been obtained which are consistent with the measured thermodynamic properties and phase diagrams as well as with established thermodynamic principles and theories of solution behavior. The parameters of these expressions are reported here and have been used to generate the computer-calculated diagrams in the compilation. The following section of this discussion describes the computer-coupled thermodynamic/phase diagram analysis used in the critical evaluation of binary phase diagram data. This procedure enables the evaluator to test the thermodynamic consistency within and among all reported phase diagram and excess property measurements. This procedure, we believe, results in a much more rigorous and objective assessment of all data than has hitherto been possible. Futhermore, it enables a thermodynamically correct smoothing of the experimental data to be performed and a "best" phase diagram to be calculated.

For each of the 124 binary systems included in this volume, the details of the evaluation procedure are given in the commentary accompanying the phase diagram for that system. Not all reported experimental points are shown on the phase diagram in each case. However, all references found for each system have been included and discussed. The evaluated equations for the thermodynamic properties of all phases are given. The phase diagrams shown were calculated from these equations and are considered to be the best evaluated diagrams which can be deduced from the data currently available. The "probable maximum inaccuracy" of the evaluated phase diagram has been estimated for each system. Phase boundaries indicated by dashed lines are considered to be less accurately known.

Ternaries

For the ternary systems, the ternary thermodynamic properties were calculated, via solution models, from the optimized values of these properties in the three binary subsystems. The ternary diagrams were then calculated from these ternary properties. Ternary diagrams calculated in this way are consistent with the assessed binary diagrams and with thermodynamic principles. The techniques used to calculate the ternary phase diagrams are described in Section 3.

Experimental liquidus surfaces have been reported for 47 of the 60 possible common-ion ternary alkali halide systems treated in the present volume. These data are of varying degrees of accuracy. For instance, the binary subsystems of a reported ternary often disagree significantly with the assessed binary diagrams. For the systems for which data are available, the thermodynamically calculated diagram was compared with the reported diagram and, in most cases, agreement was within experimental error limits. In five systems, a small empirical correction term was added to bring the calculated and reported diagrams into coincidence.

Because of the consistently excellent agreement between calculated and reported ternary diagrams in these and many other salt systems,[18] we can calculate with confidence the phase diagrams for the remaining common-ion ternary alkali halide systems for which no reported phase diagrams exist.

A calculated ternary diagram is, of course, consistent with the assessed phase diagrams of its binary subsystems. All liquidus and solidus isotherms are consistent with thermodynamic principles and with all available thermodynamic data. Solidus as well as liquidus surfaces are generated.

For each of the 60 common-ion alkali halide ternary systems in the present volume, the details of the evaluation procedure are given in the commentary accompanying the phase diagram for that system. All references found for each system are listed and discussed. The calculated ternary phase diagrams are considered to be the best evaluated diagrams which can be deduced from the data currently available. The "probable maximum inaccuracy" has been estimated for each system.

Pure Salts

In the course of the evaluations, a consistent set of melting and transformation temperatures and Gibbs energies was adopted for the pure salts. In some cases, these values were re-assessed from data in the recent literature. Details of the assessments are included here in Section 5.

In Section 4 are tabulated the temperatures and Gibbs energies of fusion and transformation of the pure salts. While most of the pure component data were taken from a recent standard source,[9] a re-evaluation using more up-to-date data was found necessary in a few cases, as indicated in Section 5. It should be noted that for all binary and ternary systems reported here, one consistent set of melting points and transformation points for the pure salts has been adopted. In

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*A similar discussion of this topic appears in J. Sangster and A. D. Pelton, *J. Phys. Chem. Ref. Data,* **16** [3] 509-561 (1987).

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many reported experimental binary and ternary phase diagrams, the melting points and transformation points of the pure salts differ significantly from these values. Account was taken of this problem in the evaluations.

Computer Programs

All computer programs form part of the F*A*C*T computer system. The interactive computer programs which were used in the optimizations and phase diagram calculations are described in Ref. 11. These programs are available "on-line" or on diskette and further information may be obtained from the authors.

2. *COMPUTER-COUPLED THERMODYNAMIC/PHASE DIAGRAM ANALYSIS OF BINARY SYSTEMS*

Introduction

As well as providing a set of self-consistent thermodynamic equations which simultaneously reproduce the thermodynamic properties and the phase diagram of the system, the technique of coupled thermodynamic/phase diagram analysis yields a thermodynamically correct "smoothing" of the experimental data. Futhermore, discrepancies among various sets of data can often be resolved in this way and error limits can more easily be assigned. Unknown or uncertain phase boundaries can often be estimated with good precision, and, conversely, some reported phase boundaries can be rejected as being inconsistent with the thermodynamic properties of the system. Finally, such a thermodynamic analysis is the first step in estimating ternary and higher-order phase diagrams from binary data. A short bibliography on computer-coupled thermodynamic/phase diagram analysis and calculation[10-18] should suffice to orient the reader. The principles of simultaneous least-squares optimization of thermodynamic and phase diagram data are described in Ref. 10. The interactive computer programs which were used in the optimizations and phase diagram calculations are described in Ref. 11.

Thermodynamic Relationships

For equilibrium between a solid and a liquid phase in a binary system with components A and B, we may write Eq. 1.

$$RT \ln a_A^{\ell} - RT \ln a_A^{s} = -\Delta_{fus}G_A^0 \qquad (1)$$

The quantities a_A^{ℓ} and a_A^{s} are the activities of A on the liquidus and solidus at temperature T. Here, $\Delta_{fus}G_A^0$ is the Gibbs energy of fusion of A at T and R is the gas constant. Setting the ideal activities equal to the mole fractions X^{ℓ} and X^{s} we may write Eq. 2.

$$RT \ln X_A^{\ell}/X_A^{s} + G_A^{E(\ell)} - G_A^{E(s)} = -\Delta_{fus}G_A^0 \qquad (2)$$

$G^{E(\ell)}$ and $G^{E(s)}$ are the partial excess Gibbs energies of A in the liquid and solid. These quantities are zero in an ideal solution. The relationship between the excess Gibbs energies and the activity coefficients, γ^{ℓ} and γ^{s}, in the liquid and solid are given in Eqs. 3 and 4.

$$G_A^{E(\ell)} = RT \ln \gamma_A^{\ell} \qquad (3)$$

$$G_A^{E(s)} = RT \ln \gamma_A^{s} \qquad (4)$$

With molten salt solutions, care must be taken in applying Eq. 2 to components which contain more than one mole of cations or anions per mole of component. For example, in the Li_2SO_4-K_2SO_4 system, each mole of Li_2SO_4 supplies two moles of Li^+ ions which mix with the two moles of K^+ ions supplied by each mole of K_2SO_4. Hence, for each component, the ideal term in Eq. 2 must be multiplied by a factor 2, as in the following example.

$$2RT \ln X_{Li_2SO_4}^{\ell}/X_{Li_2SO_4}^{s} + G_{Li_2SO_4}^{E(\ell)} - G_{Li_2SO_4}^{E(s)} = -\Delta_{fus}G_{Li_2SO_4}^0 \qquad (5)$$

On the other hand, for the system Li_2SO_4-Li_2CO_3 no factor 2 should be included since in this case it is the anions, SO_4^{2-} and CO_3^{2-}, which mix, and each mole of component Li_2SO_4 or Li_2CO_3 supplies only one mole of anions.

An equation identical to Eq. 2 can be written for the other component, B. If the Gibbs energies of fusion are known, and if the excess Gibbs energies are also known as functions of temperature and composition, then these two equations can be solved simultaneously by numerical methods to calculate the liquidus and solidus lines. Conversely, if the liquidus and solidus are known along with the excess Gibbs energies for one phase, then the excess Gibbs energies of the other phase can be calculated.

A relationship identical to Eq. 2 also applies along the phase boundaries for equilibrium between two solid phases. In this case, the Gibbs energy of fusion in Eq. 2 is replaced by the Gibbs energy of allotropic transformation.

The integral excess Gibbs energy, G^E, is related to the partial excess Gibbs energies by the following equation.

$$G^E = X_A G_A^E + X_B G_B^E \qquad (6)$$

Conversely, the partial properties can be obtained from the integral property through Eq. 7, where i = A or B.

$$G_i^E = G^E + (1 - X_i)\frac{dG^E}{dX_i} \qquad (7)$$

The excess Gibbs energy can be written as in Eq. 8, where H^E and S^E are the excess enthalpy and entropy, respectively.

$$G^E = H^E - TS^E \qquad (8)$$

In most cases, it can be assumed that H^E and S^E are independent of temperature. In only three of the 124 binary systems in the present compilation were the data of sufficient precision and available over a wide enough temperature range to merit inclusion of a temperature-dependent term in the expressions for H^E and S^E. The details are discussed in the commentaries for these particular systems. For the remainder of the present discussion, it will be assumed that H^E and S^E are independent of temperature.

Polynomial Expressions of Excess Properties

For phases (solid and liquid) with extended ranges of solubility, H^E and S^E may be expanded as polynomials in the equivalent fractions as follows.

$$H^E = (q_A X_A + q_B X_B) Y_A Y_B (h_0 + h_1 Y_B + h_2 Y_B^2 + \ldots) \qquad (9)$$

$$S^E = (q_A X_A + q_B X_B) Y_A Y_B (s_0 + s_1 Y_B + s_2 Y_B^2 + \ldots) \qquad (10)$$

The h_i and s_i are empirical coefficients. The factors q_A and q_B are the number of equivalents per mole of component. For example, q_{NaCl} = 1, $q_{K_2SO_4}$ = 2. Y_A and Y_B are the equivalent fractions as defined in Eq. 11.

$$Y_A = q_A X_A/(q_A X_A + q_B X_B) = (1 - Y_B) \qquad (11)$$

The factor $(q_A X_A + q_B X_B)$ in Eqs. 9 and 10 is the number of equivalents per mole of solution.

Although H^E and S^E could also be expressed as polynomials in the mole fractions X_A and X_B, experience has shown that expansions in terms of the equivalent fractions generally give somewhat better representations with fewer coefficients. Futhermore, in the calculation of activities in multicomponent reciprocal systems, it is an advantage if equivalent fractions are used consistently.

If $q_A = q_B = 1$, as is the case in a system of two alkali halides such as NaCl-KCl, then the equivalent fractions are identical to the mole fractions and the factor $(q_A X_A + q_B X_B)$ is equal to unity. In such cases, we have usually simply written Eqs. 9 and 10 as polynomials in X_A and X_B.

Expressions for the partial properties can be obtained by differentiating Eqs. 9 and 10 via Eq. 7 to give the following equations.

$$H_A^E = q_A \sum_{i=0} h_i (Y_B - iY_A) Y_B^{i+1} \tag{12}$$

$$S_A^E = q_A \sum_{i=0} s_i (Y_B - iY_A) Y_B^{i+1} \tag{13}$$

$$H_B^E = q_B Y_A^2 \sum_{i=0} h_i (i+1) Y_B^i \tag{14}$$

$$S_B^E = q_B Y_A^2 \sum_{i=0} s_i (i+1) Y_B^i \tag{15}$$

Using the preceding equations, the following quantities are derived.

$$G_A^E = RT \ln \gamma_A = H_A^E - TS_A^E \tag{16}$$

$$G_B^E = RT \ln \gamma_B = H_B^E - TS_B^E \tag{17}$$

The empirical coefficients h_i and s_i are found by the simultaneous optimization of the thermodynamic and phase diagram data. If only the first terms, h_0 and s_0, in the empirical series Eqs. 9 and 10 are nonzero, then the solution is termed "regular". If two terms are required to fit the data, then the system is called "subregular". Experience has shown that most common-ion molten alkali salt solutions approximate quite closely to regular or subregular behavior. No more than three terms were required in Eqs. 9 and 10 for any of the 124 systems in the present compilation and usually one or two terms sufficed. If only limited experimental data are available, then the assumption of regular or subregular behavior will yield an acceptable approximation.

Experience with molten alkali salt solutions has also shown that the enthalpic term H^E in Eq. 8 is generally larger in absolute magnitude than the entropic term TS^E. Hence, if available data are limited, it is a reasonable assumption to set $S^E = 0$ and to assume that G^E is temperature independent.

As a general rule, the larger the radius of the cations and/or anions and the smaller the difference between the radii of the two cations in a common-anion binary system (or between the two anions in a common-cation binary system), the more closely the above approximations (one- or two-term polynomial expansions; $S^E = 0$) are obeyed.

Solid Solutions with Limited Solubility: Henrian Behavior

In certain systems, limited solid solubility of only a few mole percent of one component in the other is observed. Such solid solutions may be considered to be Henrian solutions. That is, letting component A be the solvent, the activity of A is ideal (Raoultian).

$$a_A^s = X_A^s \text{ and } G_A^{E(s)} = 0 \tag{18}$$

For the solute, B, the activity coefficient $\gamma_B^s = a_B^s / X_B^s$ is independent of composition. Hence, $G_B^{E(s)} = RT \ln \gamma_B^s$ is also independent of composition, and can, to a reasonable approximation, be taken to be independent of temperature.

$$G_B^{E(s)} = RT \ln \gamma_B^s = \text{constant} \tag{19}$$

In a few systems, a linear temperature dependence of $G_B^{E(s)}$ has been assumed.

In such cases of limited solid solubility of solute B in solvent A, we note that Eq. 2 alone is sufficient to permit $G_A^{E(\ell)}$ to be calculated along the liquidus, if the solidus and liquidus lines are known, since $G_A^{E(s)} = 0$.

Limiting Slopes of Liquidus Lines: Estimation of Solid Solubility

In some systems, the extent of solid solubility is not known. In such cases, the measured limiting slope of the liquidus line (dX^ℓ/dT) at $X^\ell = 1$ (pure A) can permit the extent of solid solubility to be estimated. In the limit at $X_A = 1$, both the liquid and solid phases become Henrian such that $G_A^{E(s)}$ and $G_A^{E(\ell)}$ both approach zero. Similarly, for $X_A \approx 1$, the Gibbs energy of fusion of A is well approximated by the expression $\Delta_{\text{fus}} H_A^0 (1 - T/T_{\text{fus(A)}})$ where $\Delta_{\text{fus}} H_A^0$ is the enthalpy of fusion of A at its melting point, $T_{\text{fus(A)}}$. Differentiation of Eq. 2 in the limit at $X_A = 1$ then yields Eq. 20.

$$\frac{dX_A^\ell}{dT} - \frac{dX_A^s}{dT} = \frac{\Delta_{\text{fus}} H_A^0}{R (T^0_{\text{fus(A)}})^2} \text{ when } X_A = 1 \tag{20}$$

(In the case of a salt such as A = Na_2SO_4 in the system Na_2SO_4-K_2SO_4 where each mole of A yields two moles of Na^+ ions, a factor 2 must be involved in the denominator on the right-hand-side of Eq. 20.)

From the known enthalpy of fusion and the measured limiting liquidus slope, dX^ℓ/dT, the limiting solidus slope, dX^s/dT, can be calculated. If this slope is close to zero, then the solid solubility is of limited extent.

Optimization Procedure

The actual steps followed in an optimization will vary from system to system. Details are given in the commentary for each system. However, some general observations can be enunciated.

In 71 of the 124 binary systems in the present volume, $H^{E(\ell)}$ in the liquid phase has been measured calorimetrically, usually by Prof. O. Kleppa and co-workers. These data, which are generally very reliable, have been fitted to one-, two-, or three-membered series as in Eq. 9.

In the cases of systems with limited solid solubility, Eq. 2 was then used under the assumption of Henrian solid behavior to calculate excess Gibbs energies along the A- and B-liquidus lines. That is, $G_A^{E(s)}$ was set equal to zero for the solvent, according to Eq. 18. Combining these excess Gibbs energies with the already-fitted calorimetric liquid enthalpies permitted the excess liquid entropy $S^{E(\ell)}$ to be calculated and then smoothed by representation as a one- or two-member (very exceptionally a three-member) polynomial as in Eq. 10. The Henrian constant of Eq. 19 could then be calculated from the measured solubility limits for each of the two solid solutions. In those few systems for which calorimetric liquid enthalpies were not available, $S^{E(\ell)}$ was set equal to zero, and the values of $G^{E(\ell)} = H^{E(\ell)}$ obtained from the phase diagram were then smoothed by polynomial representation as in Eq. 9.

In those systems with complete solid miscibility, $H^{E(s)}$ has been measured calorimetrically in only a few cases. In general, in these systems it must be assumed that $S^E = 0$ in either the liquid or solid phase or in both. If $G^{E(s)}$ for the completely miscible solid phase is positive, then there will be a zone of demixing (i.e., a miscibility gap) in the solid, whose boundaries and consolute point can be calculated from the equation for $G^{E(s)}$. Conversely, if the miscibility gap has been measured experimentally, then these data can be used to help determine the coefficients in the expression for $G^{E(s)}$.[10]

Some of the systems studied contain intermediate compounds. In only two cases have the Gibbs energies of fusion of these compounds been measured. However, once $H^{E(\ell)}$ and $S^{E(\ell)}$ have been determined, the Gibbs energies of fusion of the compounds can be calculated from their measured liquidus lines via Eq. 2 if they are assumed to be stoichiometric compounds. Their Gibbs energies of formation from the pure component salts can then also be calculated.

In a few systems, activities of components have been measured by auxiliary methods. The number of such systems is small. The following is a summary showing the number of binary systems out of the 124 in the present study for which different data types were available.

Systems with phase diagram and/or thermodynamic data	121
Systems with EMF (electromotive force) data	7
Systems with vapor pressure data	2
Systems with mass spectrometric data	2

For all those systems having auxiliary data, the pertinent sources are mentioned and discussed in the commentary for the appropriate system, and all references have been retained. These data also could be used, in principle, in the data optimization but were, in fact, not used because they were too sparse or inaccurate. That is, we favored phase diagram and thermodynamic data in our optimization and excluded other types of data because the latter were few and uncertain. Electromotive force measurements in systems containing alkali metals are particularly difficult due to spurious effects. The interpretation of vapor pressure data is not entirely unambiguous and precise measurement is difficult. The mass spectrometric data may be accurate, depending upon the species whose ion currents are used to derive activities.

Only in the case where no phase diagram or thermodynamic data were at hand, but auxiliary data were available, would we consider the use of auxiliary data in the optimization. This case never occurred among the 124 binary systems reported here. In such a hypothetical case, auxiliary data would be considered together with qualitative and quantitative estimates drawn from phase diagram and thermodynamic properties of analogous systems already studied.

3. *COMPUTER CALCULATION OF TERNARY PHASE DIAGRAMS*

A short bibliography on the computer calculation of ternary diagrams is given in Refs. 11-18.

In the thermodynamic approach, the Gibbs energy of a ternary solution phase is estimated from the optimized Gibbs energies of the three binary subsystems. The ternary diagram is then calculated from the estimated Gibbs energies. If experimental ternary data are available, these may be used to refine the calculations. The interactive computer program used to calculate the ternary phase diagrams is described in Ref. 11.

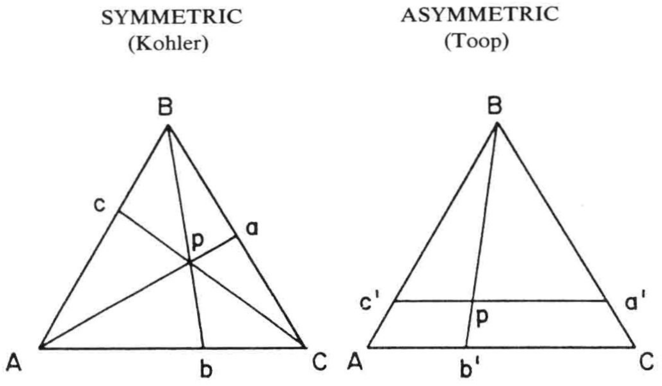
In the case of simple common-ion ternary molten salt solutions in which G^E of the binaries can be well represented by simple polynomial expansions, certain "geometric" models, which are based upon regular solution theory, have proved successful in estimating ternary properties from binaries. Two of these are illustrated in Fig. 1.

In the "symmetric" or "Kohler" equation, G^E at point "p" in the ternary is related to the binary values at points a, b, and c. The symmetric (Kohler) approximation is given in Eq. 21, where X_A, X_B, and X_C are the component mole fractions.

$$G_p^E = (1 - X_C)^2 G_c^E + (1 - X_A)^2 G_a^E + (1 - X_B)^2 G_b^E \qquad (21)$$

The "asymmetric" or "Toop" equation, also illustrated in Fig. 1, is given in Eq. 22.

$$G_p^E = [X_A/(X_A + X_C)]G_c^E + [X_C/(X_A + X_C)]G_a^E + (1 - X_B)^2 G_b^E \qquad (22)$$


SYMMETRIC
(Kohler)

ASYMMETRIC
(Toop)

Fig. 1. Gibbs triangle for a common-ion ternary system illustrating the geometrical relationships involved in the symmetric (Kohler) equation[21] and the asymmetric (Toop) equation.[22]

In the general case, equivalent fractions Y_i should replace the mole fraction X_i in Eqs. 21 and 22 and the excess Gibbs energies should refer to one equivalent of solution. However, in the present volume, we report on only common-ion alkali halide ternaries in which mole fractions and equivalent fractions are identical.

The factors multiplying each binary excess Gibbs energy in Eqs. 21 and 22 are obtained from regular solution theory such that Eqs. 21 and 22 are exact if the ternary solution is strictly regular. The symmetric approximation is more appropriate when all three components are common-ion salts of the same valence (e.g., NaCl-KCl-LiCl), whereas the asymmetric approximation is recommended for systems such as KCl-$MgCl_2$-$CaCl_2$ where one salt, KCl, has ions of a valency different from the other two. In this case, the odd salt becomes component B in Fig. 1. The asymmetric approximation is also more appropriate for a ternary solid solution in which components A and C are miscible at all concentrations but in which B is only sparingly soluble. Other geometric equations based on regular solution theory have been proposed. For example, in the "Muggianu" method, G^E at the ternary point "p" is related to values of G^E in the three binaries at the ends of perpendiculars dropped from point "p" to the binaries. These equations have been reviewed.[19] Generally, in the salt systems in the present volume, all these methods yield very similar results.

The reason that simple equations such as Eqs. 21 and 22, which are based on the regular solution model, give good predictions in ionic systems is that the basic assumptions of regular solution theory (additivity of pair-bonded energies, small excess entropy) are satisfied in ionic systems in which coulombic forces predominate.

When some experimental ternary data of sufficient accuracy are available, then these can be used to refine the calculations through the addition of ternary correction terms to the Gibbs energy expression in Eqs. 21 or 22. In the few cases in the present study in which a ternary correction term was deemed to be justified, one term of the form $aX_AX_BX_C$ was sufficent. This term is necessarily zero in any binary subsystem. The coefficient "a" was chosen to bring the calculated and reported diagrams into coincidence.

4. *THERMODYNAMIC DATA FOR PURE SALTS*

Temperatures of fusion (T^0_{fus}) or phase transformation (T^0_{trs}) and Gibbs energies of fusion ($\Delta_{\text{fus}}G^0$) or phase transformation ($\Delta_{\text{trs}}G^0$) of pure salts.*

$$\Delta_{\text{fus}}G^0 \text{ or } \Delta_{\text{trs}}G^0 = a + bT + cT^2 + dT \ln T + e/T \text{ (J·mol}^{-1}\text{)}$$

Salt	I→II	T^0_{fus} or T^0_{trs} (*K*)	$a \times 10^{-3}$	*b*	$c \times 10^3$	*d*	$e \times 10^{-5}$
LiF	$s \to \ell$	1121	14.518	128.435	8.709	−21.494	−2.65
NaF	$s \to \ell$	1269	10.847	156.584	4.950	−23.978	−1.07
KF	$s \to \ell$	1130	13.763	127.035	7.211	−20.962	0
RbF	$s \to \ell$	1066	2.388	251.453	19.268	−39.367	2.51
CsF	$s \to \ell$	976	3.451	176.219	8.872	−27.372	0
LiCl	$s \to \ell$	883	4.420	197.318	16.435	−31.966	0
NaCl	$s \to \ell$	1074	7.735	202.091	11.925	−31.824	0
KCl	$s \to \ell$	1044	4.755	215.399	12.734	−33.581	1.82
RbCl	$s \to \ell$	993	7.759	96.729	5.209	−15.899	0
CsCl	$\alpha \to \beta$	743	−1.806	87.773	8.580	−13.874	0
	$\beta \to \ell$	918	1.755	116.390	2.469	−17.673	0
LiBr	$s \to \ell$	823	2.079	215.437	20.682	−35.070	2.97
NaBr	$s \to \ell$	1020	18.327	75.124	6.657	−14.418	0
KBr	$s \to \ell$	1007	10.483	160.372	11.335	−26.349	0
RbBr	$s \to \ell$	967	10.054	110.999	5.335	−18.410	0
CsBr	$s \to \ell$	908	1.890	189.667	5.419	−28.874	0
LiI	$s \to \ell$	742	6.591	121.310	14.046	−21.275	0
NaI	$s \to \ell$	933	13.940	88.680	6.027	−15.975	0
KI	$s \to \ell$	954	4.656	211.209	14.460	−33.547	2.46
RbI	$s \to \ell$	920	12.280	107.227	5.502	−18.410	0
CsI	$s \to \ell$	913	48.639	−358.103	−21.213	47.488	4.04
$LiNO_3$	$s \to \ell$	528	25.563	−48.415	0	0	0
$NaNO_3$	$\alpha \to \beta$	550	4.420	−8.036	0	0	0
	$\beta \to \ell$	583	15.177	−26.033	0	0	0
KNO_3	$\alpha \to \beta$	403	5.110	−12.680	0	0	0
	$\beta \to \ell$	610	10.129	−16.605	0	0	0
LiOH	$s \to \ell$	750	20.962	−27.949	0	0	0
NaOH	$\alpha \to \beta$	570	6.360	−11.158	0	0	0
	$\beta \to \ell$	593	6.360	−10.725	0	0	0
KOH	$\alpha \to \beta$	522	6.339	−12.144	0	0	0
	$\beta \to \ell$	677	9.372	−13.843	0	0	0
Li_2SO_4	$\alpha \to \beta$	851	25.650	−30.141	0	0	0
	$\beta \to \ell$	1133	8.990	−7.935	0	0	0
Na_2SO_4	$\alpha \to \beta$	520	10.811	−20.790	0	0	0
	$\beta \to \ell$	1157	23.012	−19.889	0	0	0
K_2SO_4	$\alpha \to \beta$	856	8.954	−10.460	0	0	0
	$\beta \to \ell$	1342	36.819	−27.436	0	0	0
Li_2CO_3	$\alpha \to \beta$	683	2.238	−3.277	0	0	0
	$\beta \to \ell$	1003	44.769	−44.635	0	0	0
Na_2CO_3	$\alpha \to \beta$	632	0.368	−0.582	0	0	0
	$\beta \to \gamma$	758	2.536	−3.346	0	0	0
	$\gamma \to \ell$	1131	29.665	−26.229	0	0	0
K_2CO_3	$\alpha \to \beta$	695	0.230	−0.331	0	0	0
	$\beta \to \ell$	1174	27.614	−23.521	0	0	0

---

* Data have been taken from the standard reference[9] unless otherwise indicated in the following section, "Revision of pure salt thermodynamic properties".

5. *REVISION OF PURE SALT THERMODYNAMIC PROPERTIES*

Fluorides

RbF

The melting point of RbF is that of Holm[20], who took particular care in its purification. The enthalpy of fusion at this temperature is 22 930 J·mol^{-1}, obtained from heat content measurements.[21]

Chlorides

RbCl

The melting point of RbCl has been updated.[22]

Bromides

RbBr

The melting point has been updated.[23] The enthalpy of fusion has been taken to be 22 868 J·mol^{-1}. This corrected value was obtained from the entropy of fusion 23.648 J·mol^{-1}·K^{-1}, estimated by an interpolative method.[24,25]

Iodides

RbI

The melting point has been revised upward, and a more recent representative value was taken from a standard handbook.[26] The calorimetric value for the enthalpy of fusion, 24 560 J·mol^{-1}, has been used.[27]

CsI

The melting point has been revised upward.[28]

Nitrates

$LiNO_3$

The standard reference[9] contains no data for this compound. A survey of binary phase diagrams containing $LiNO_3$ in two large compilations[1,7] revealed melting points in the range 244°-270°C; more careful work on the salt itself[29-32] indicated 253°-255°C. The value 255°C was chosen for the present work. Calorimetric determinations of the enthalpy of fusion[30-34] indicated values between 24 940 and 26 740 J·mol^{-1}; a mean value of 25 563 J·mol^{-1} was used here.

$NaNO_3$

The standard reference[9] contains no data on the solid state transition. Recent reports of the transition temperature[31,32,35-40] give values between 262° and 277°C; the most recent value, 277°C,[36] was adopted here. Calorimetrically determined enthalpies of transition[31,35,36,40] vary between 689 and 4686 J·mol^{-1}; again, the most recent value[36] of 4420 J·mol^{-1} was used here.

The melting point of $NaNO_3$ has been revised upward[29,30,36,37] to 310°C. For the enthalpy of fusion, calorimetrically determined values communicated both before[30-33,38,39,43,44] and after[35,41,42] the appearance of the standard reference[9] suggested the slightly higher value of 15 177 J·mol^{-1} used in this work.

KNO_3

The phase transition temperature has been revised upward to 130°C[36,40,42] and the melting point to 337°C.[30,35,36,45] For the enthalpy of transition, the most recent[42] value of 5110 J·mol^{-1} was used. Calorimetrically determined enthalpies of fusion[30,32,33,35,37,43] vary between 9205 and 10 753 J·mol^{-1}, and a slightly higher value of 10 129 J·mol^{-1} was used in the present work.

Hydroxides

LiOH

The melting point has been revised upward to 477°C.

NaOH

The phase transformation temperature has been revised upward to 297°C.

KOH

The melting point has been revised upward to 404°C.

Sulfates

Li_2SO_4

Although the standard reference[9] lists the phase transition temperature as 586°C, careful work on the pure substance,[42,46-51,64] as well as values reported in binary phase diagram data,[1,7] indicate a temperature in the range 572°-579°C. In the present work, 578°~~C was~~ adopted. Calorimetric determinations[42,46-48,52,64] of the enthalpy of transition indicate values between 24 200 and 28 880 J·mol^{-1}. A slightly revised enthalpy of 25 650 J·mol^{-1} is used here. The melting point was taken to be 860°C.[48,53] The enthalpy of fusion quoted in the standard reference[9] is 13 800 J·mol^{-1}, but three independent determinations, 8990 J·mol^{-1}, 7740 J·mol^{-1}, and 7669 J·mol^{-1} (Refs. 48, 64, and 52, respectively), suggest a rather different magnitude. It was found that the most recent[48] value of 8990 J·mol^{-1} was more consistent with all the binary phase diagrams containing Li_2SO_4 which were critically evaluated. This value was, therefore, retained in this work.

Na_2SO_4

The reported polymorphism of Na_2SO_4 indicates a number of structural modifications[53,54] but some of these are metastable. For the purposes of this critical evaluation of binary phase diagrams, it sufficed to retain only the well-established transition at 247°C.

Carbonates

Li_2CO_3

The reported polymorphism of Li_2CO_3, as determined by thermal analysis, includes a number of apparent transition temperatures, although investigators do not agree on their status. Reisman[55] discovered that some are spurious due to impurities (LiOH, Li_2O) introduced by decomposition or the presence of water. The analysis should, therefore, be done under a dry CO_2 atmosphere.[55,56] For present purposes, one transition at 410°C is retained and the enthalpy of transition is taken from the standard reference.[9] The melting point has been revised upward to 730°C.[48] The most recently determined[48] enthalpy of fusion, 73 400 J·mol^{-1}, is not consistent with the same authors' phase diagram data[48] for Li_2CO_3-Li_2SO_4, and so the value from the standard reference,[9,56] 44 770 J·mol^{-1}, was used instead.

Na_2CO_3

The same confusion concerning apparent phase transitions in Li_2CO_3, described above, applies to Na_2CO_3.[57] For present purposes, two transition temperatures were retained: 359°C and 485°C, after Janz and Perano.[58] These temperatures are within 5°C of other independent measurements.[57,59-61] The enthalpies of transition were also taken from Ref. 58. The melting point has been revised upward to 858°C.[56]

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K_2CO_3

The same confusion concerning apparent phase transitions in Li_2CO_3, described above, applies to K_2CO_3.[55] For present purposes, one phase transition at 422°C[55,58,60] was retained. Although this transition has been called second-order[62,63] with zero enthalpy, volume, and crystal structure change, its manifestation in a phase diagram clearly indicates otherwise. The enthalpy of transformation reported by Janz and Perano[58] was used.

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Table of Contents

A. Metal Plus Halides or Halogens

I. One Metal Plus One Bromide

Bi-BiBr$_3$

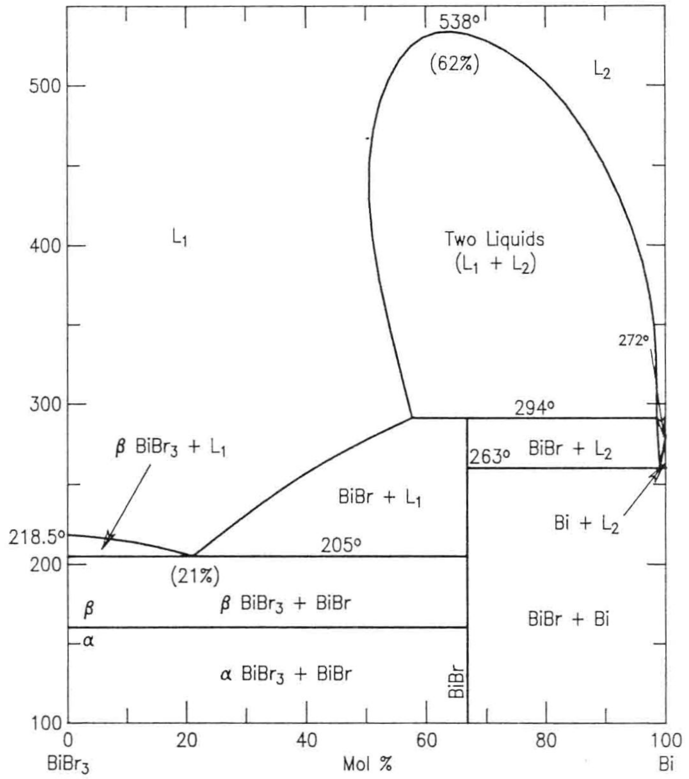

Fig. **6952**—System BiBr$_3$-Bi.

S. J. Yosim, L. D. Ransom, R. A. Sallach, and L. E. Topol, *J. Phys. Chem.*, **66**, 28-31 (1962).

STARTING MATERIALS: Bi was prepared from reagent-grade Bi, melted under an inert atmosphere, and filtered through glass wool to yield a shiny ingot with a melting point of 271.0°C. BiBr$_3$ was prepared by exposing liquid Bi to Br vapor from a bromine reservoir; the salt was subsequently sublimed to yield material with a melting point of 218.5°C. Chemical analysis showed 46.5 wt% Bi (vs 46.57% theoretical).

STARTING COMPOSITIONS: At least 18 mixtures, distributed more or less uniformly across the diagram.

CONTAINMENT: Vycor, fused silica, or Pyrex were used.

APPARATUS AND TECHNIQUE: The miscibility gap was studied by decanting and chemically analyzing the salt-rich layer, by DTA, and by visual observation (metal-rich side). The subsolidus was studied using DTA. The lower temperature part of the liquidus was studied by decantation. For the DTA experiments, Chromel-Alumel thermocouples were inserted in a well in the glass cells. Use of a rocking furnace allowed continuous mixing of the samples in all experiments.

CHARACTERIZATION: Chemical analysis of decanted material.

SPECIAL POINTS: The authors indicate a critical point at 538°C, 62 mol% Bi.

DISCUSSION: The authors conclude that the solid subhalide BiBr exists, in agreement with Refs. 1 and 2. The authors interpret extension of eutectic DTA effects in both directions beyond the BiBr composition as due to metastability. No X-ray data for this system are reported, and the existence of BiBr is inferred partly on the basis of analogy with the Bi-BiCl$_3$ system (Fig. 1658). Results of a cryoscopic analysis of the liquidus are discussed. For a more recent determination of the miscibility gap and the effect of pressure, refer to Figs. 6953 and 6954.

1. B. G. Eggnik, *Z. Phys. Chem.*, **64** [4] 449 (1908).
2. G. G. Urazov and M. A. Sokolova, *Akad. Nauk SSSR, Inst. Gen. Inorg. Chem.*, **24**, 151 (1954).

L.P.C.

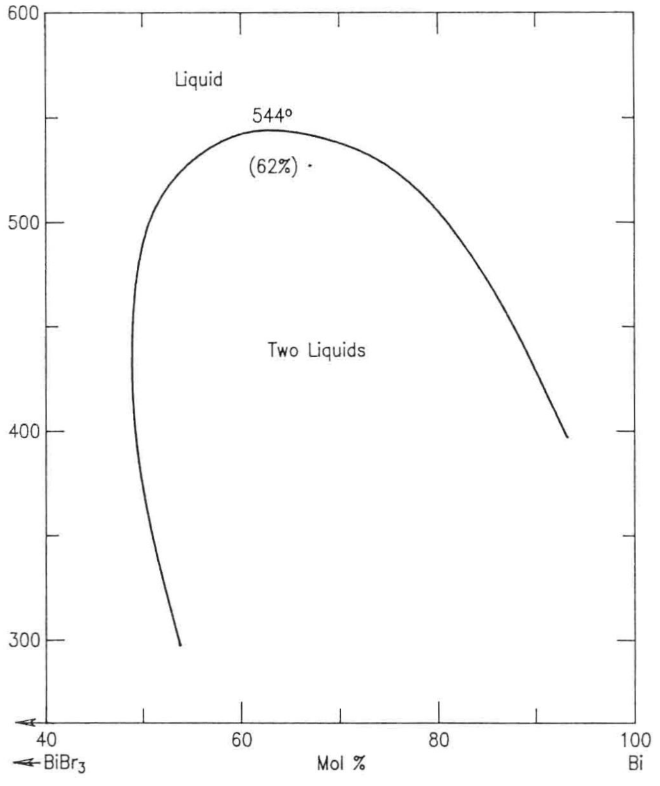

Fig. **6953**—System BiBr$_3$-Bi.

H. Hoshino, K. Tamura, and H. Endo, *Solid State Commun.*, **31** [9] 687-689 (1979).

STARTING MATERIALS: Bi of 99.999% purity (metals basis) and BiBr$_3$ purified by subliming the reagent-grade salt under reduced pressure were used. Starting mixtures were obtained by homogenizing in a rocking furnace at 590°C, followed by annealing at 580°C for 12 h.

STARTING COMPOSITIONS: Fourteen mixtures, distributed about evenly between 30 and 100 mol% Bi.

CONTAINMENT: Evacuated Pyrex cells were used.

Bi-BiBr$_3$ (cont.)

APPARATUS AND TECHNIQUE: The electrical conductivity of samples in sealed Pyrex cells was measured using tungsten electrodes calibrated against distilled mercury; temperature drop along the cells was <0.1°C. Temperature was measured using Chromel-Alumel thermocouples to within 1%.

CHARACTERIZATION: By *in-situ* study of electrical conductivity as a function of temperature; discontinuous changes in the conductivity were used to delineate the phase boundary.

SPECIAL POINTS: The critical point was determined to be at 544.0° ± 0.5°C, and 62.0 ± 0.1 mol% Bi.

DISCUSSION: This diagram represents a somewhat more detailed version of the 100 kPa (1 atm) miscibility gap than given in Fig. 6952. The 100 kPa (1 atm) position of the critical point is about 6°C higher than that given in Fig. 6952. The effect of pressure on the miscibility gap is given in Fig. 6954.

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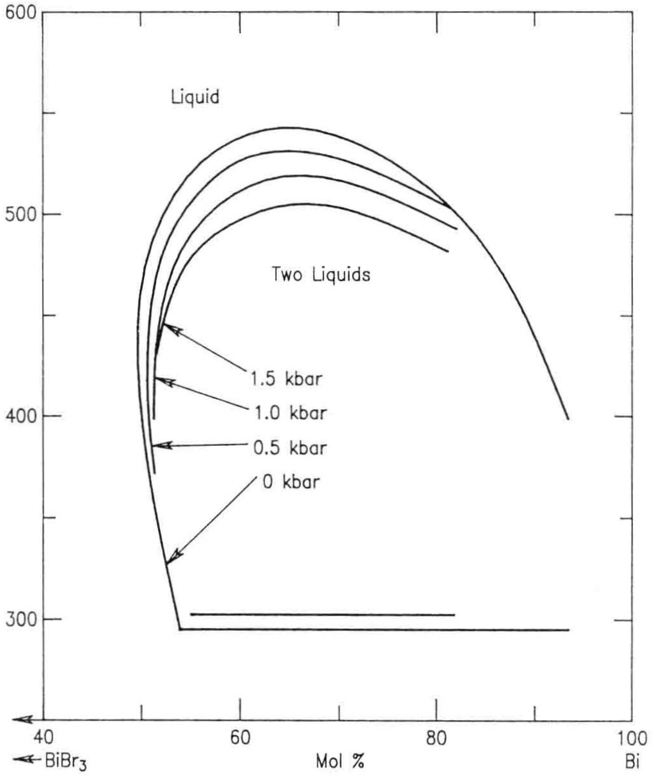
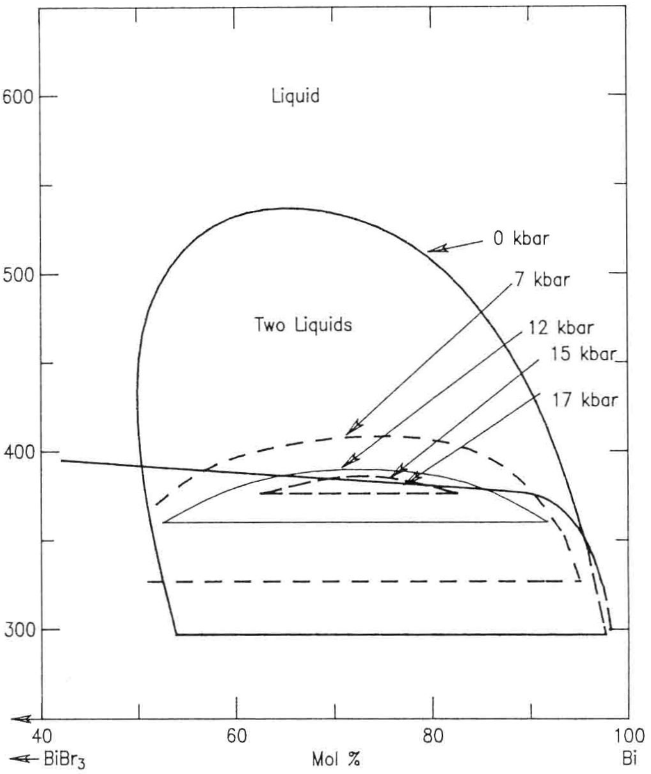
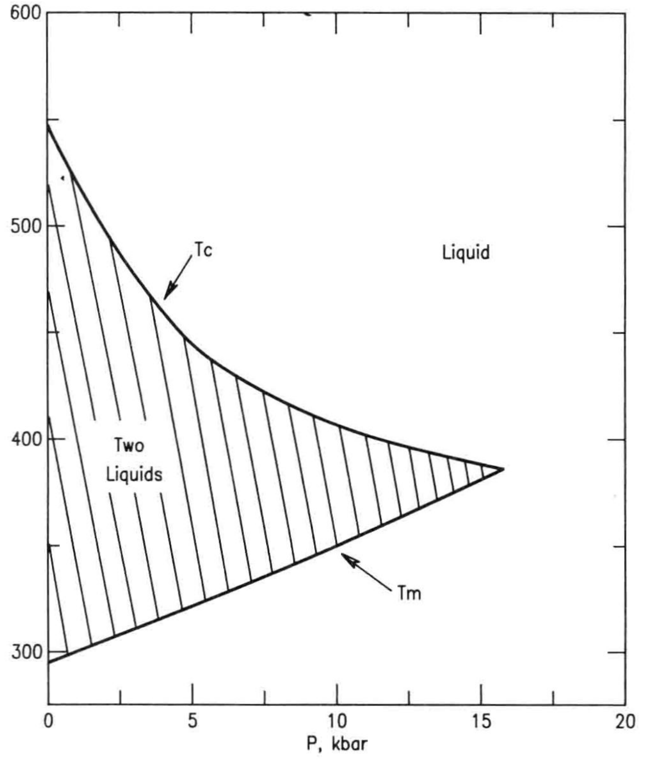
(A)



(B)



(C)



Bi-BiBr$_3$ (concl.)

Fig. **6954**—System BiBr$_3$-Bi. (*A*) Effect of pressure on the miscibility gap up to 1.5 kbar; (*B*) up to 17 kbar; (*C*) effect of pressure on the critical and monotectic temperatures. T_c = critical temperature; T_m = monotectic temperature.

K. Tamura, H. Hoshino, and H. Endo, *Ber. Bunsenges. Phys. Chem.*, **84** [3] 235-240 (1980).

H. Hoshino, K. Tamura, S. Hosokawa, K. Suzuki, M. Misonou, and H. Endo, *J. Phys., Colloq. (Orsay, Fr.)*, No. C8, 52-55 (1980).

STARTING MATERIALS: Bi (99.99%) and BiBr$_3$, purified to 99.99% by sublimation of reagent-grade salt.

STARTING COMPOSITIONS: At least six mixtures, distributed across the two-phase region; compositions stated as accurate to ±0.2 mol%.

CONTAINMENT: Up to 1.5 kbar, a Pyrex liner with tungsten electrodes was used; from 4 to 20 kbar, a fired pyrophyllite cell (900°C under vacuum, 2 h) was used, with molybdenum electrodes, and niobium end caps.

APPARATUS AND TECHNIQUE: Up to 1.5 kbar, conductivity was studied using an externally heated autoclave with argon pressure medium; mixtures were homogenized by rocking the autoclave above the critical temperature. From 4 to 20 kbar, conductivity was measured using a piston-cylinder apparatus with a graphite heater; homogeneous starting mixtures were obtained by pretreatment at 18 kbar and 600°C.

CHARACTERIZATION: By *in situ* study of electrical conductivity as a function of *P-T*; discontinuities were used to delineate phase boundaries.

SPECIAL POINTS: Refer to diagram (*C*) for the shift in critical and monotectic temperatures with pressure. The temperature of the critical point is lowered with increasing pressure, and its composition becomes more Bi rich (~73 mol% at 15 kbar); with increasing pressure the monotectic temperature increases; at 17 kbar the two-phase region has vanished.

DISCUSSION: Retrograde solubility on the BiBr$_3$-rich limb decreases rapidly with increasing pressure and disappears at about 1.5 kbar. The authors postulate structural changes in the melt to account for an inflection at high pressure in the conductivity/temperature curve near the 50 mol% composition, and imply that this may relate to the existence of BiBr$_3$ in the melt.

L.P.C.

II. One Metal Plus One or More Chlorides

Au-AuCl$_3$

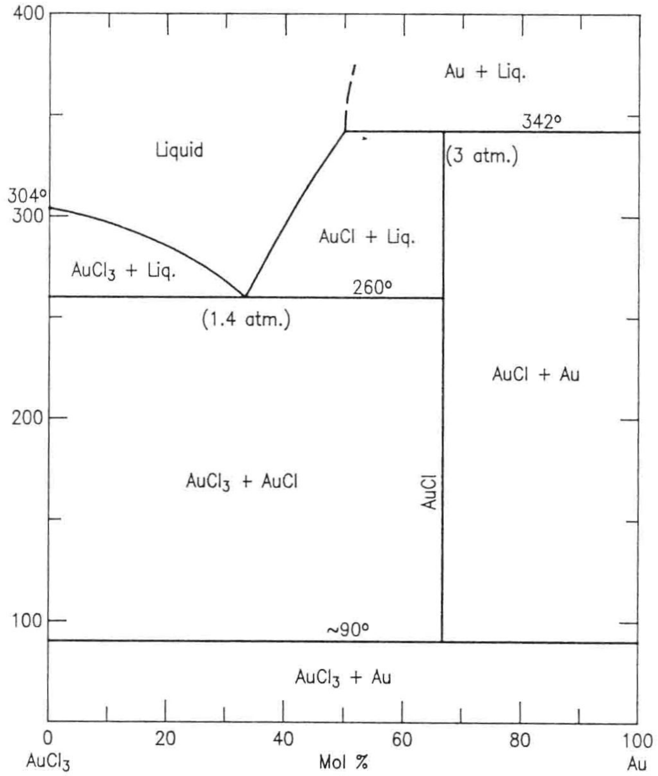


Fig. **6955**—System AuCl$_3$-Au (Chlorine pressures are calculated.)

E. M. W. Janssen, F. Pohlmann, and G. A. Wiegers, *J. Less-Common Met.*, **45** [2] 261-273 (1976).

STARTING MATERIALS: Powdered Au metal and crystalline AuCl$_3$.

STARTING COMPOSITIONS: At least 15 mixtures of the end-members, distributed primarily between AuCl$_3$ and AuCl.

CONTAINMENT: Sealed silica glass ampules (DTA) and silica glass capillaries (high-temperature X-ray) were used.

APPARATUS AND TECHNIQUE: For DTA, silica glass in a sealed ampule was the reference, and heating rates of 4.3° and 15°C/min were used. For high-temperature X-ray, patterns of AuCl were taken with a Guinier camera.

CHARACTERIZATION: No additional information given.

DISCUSSION: The melting point of AuCl$_3$ is determined from extrapolation of the liquidus; an estimate of the enthalpy of melting is given. The authors review literature evidence for existence of a compound with composition AuCl$_2$ and conclude that this material is not a compound but a eutectic mixture. Chlorine pressures for this equilibrium and the peritectic decomposition of AuCl are calculated from thermodynamic data. Other vapor species are present in these equilibria, however. According to Ref. 1 the dominant binary vapor species is Au$_2$Cl$_6$ below about 480°C and Au$_2$Cl$_2$ above that temperature.

1. S. E. James and J. P. Hager, *Metall. Trans., B*, **9** [1] 501 (1978).

L.P.C.

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