# Electrochemical Determination of Phase Diagrams and Thermodynamic Data of Multi-Component Systems

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The coulometric titration technique is extended to treat general cases of systems of any number of components. Complete equilibrium phase diagrams and thermodynamic properties are obtained from readily and precisely measurable electrical quantities, employing only a small number of samples. General equations are derived which directly relate the cell voltage to the standard Gibbs energies, enthalpies and entropies of formation of all phases involved without the necessity of considering specific cell reactions. The application of the technique to the ternary system Cu – Ge – O is demonstrated.

## I. Introduction

Phase diagrams and thermodynamic data are fundamental in materials characterization. These two properties are usually studied in separate experiments, and with much difficulty. For the determination of equilibrium phase diagrams, a large number of samples of various atomic ratios must be annealed in order to completely cover the compositional field using static methods. Structure sensing procedures, e. g X-ray diffraction or microscopic observations, are then commonly employed to examine the quenched samples. Dynamic methods can also be applied, such as the measurement of the specific heat of various compositions as the temperature is varied. An extensive literature is available containing detailed descriptions of such techniques, e. g. [1 – 3].

Under certain circumstances the number of sample preparations may be reduced by providing an exchange of one of the components by equilibration with an otherwise inert surrounding auxiliary phase. As an example, the resulting change in composition may be evaluated using a thermogravimetric technique employing a sensitive balance [4, 5]. Though it is in principle generally applicable, this technique is practically restricted to only a few atomic species, in particular to oxygen, nitrogen and sulphur. In addition, because of singularities in the thermodynamic properties of the $N$-phase regions of an $N$-component system (i. e., the activities of all components are fixed at specific values of temperature and pressure), in practice only 1- to ($N$-1)-phase regions may be observed in thermodynamic equilibrium. The usually large $N$-phase regions are not accessible. On the other hand, the resolution of a balance may not be sufficient to quantitatively investigate the often comparatively narrow ranges of existence of regions with less than $N$ phases. Also, the activity of the component which is controlled by the auxiliary surrounding phase, may only vary by a small amount from one detectable 1- to ($N$-1)-phase region to the next, and existing phases may thus remain undetected.

In contrast to this gravimetric method, the roles of the dependent and independent variable, i. e. the composition of the sample and the activity of one component, may be inverted by employing electrochemical techniques. The concentration of one (or more) of the atomic species of the sample is changed by coulometric titration whereas its resulting activity is determined simultaneously by use of a single galvanic cell. All regions that contain $1, 2, \ldots,$ or $N$ phases are accessible in this way. Due to the precision in determining electric currents, even "line" phases with extremely small compositional variations may be resolved. In addition to the phase diagram, thermodynamic information related to the formation of the various phases present is obtained without performing further experiments. The precision of electrochemically determined thermodynamic data greatly exceeds that of other techniques [6 – 9]. Only electric quantities

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need to be determined, and that can be done easily and precisely. The technique is primarily restricted only by the availability of compatible electrolytes for the appropriate species. The opportunities for its widespread use are quite good, however, since either liquid electrolytes (e. g. aqueous solutions or molten salts) or solid electrolytes may be used.

Besides the determination of phase diagrams and the determination of related thermodynamic data, this general experimental process has important practical implications. Such titrations of one of the components into or out of a sample (of any number of components) actually occurs in battery electrodes during charge and discharge processes. The phases formed in this way may be readily investigated by the technique described here.

The change of composition with the help of an auxiliary electrolyte ("coulometric titration") was introduced by Wagner [10] for binary systems, with one of the components being the electroactive one. Similar experiments have been performed subsequently with a number of other systems [11 – 37]. Usually, only the stoichiometry of single phases has been changed. Only in a few cases, the complete range of compositions of binary systems has been studied [8, 35, 36]. This information, i. e. the exact stoichiometries of all phases, is necessary for a correct calculation of thermodynamic data [5, 6].

Coulometric titration has also been applied to a few ternary compounds [15, 17, 19, 22, 25, 26, 31, 37, 38] in attempts to determine their phase widths. These results may, however, be erroneous because this method does not always distinguish between 1- and 2-phase regions, thus implying wider ranges than really exist. When only thermodynamic properties were of interest, static electrochemical methods have been employed in some cases by using 3-phase mixtures in order to fix all component activities [39 – 42]. Problems also arise in this type of experiment when the solutions of the compounds in each other are not negligible. A satisfactory situation is only reached when the phase diagram is precisely known. The method described here is therefore also of importance for pure thermodynamic studies.

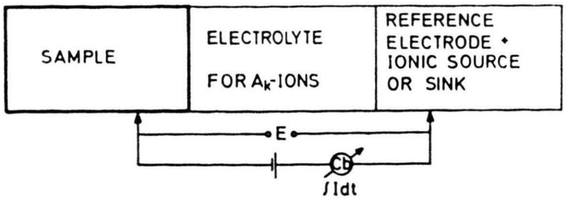

Fig. 1. Schematic representation of the galvanic cell employed for studying phase equilibria and the thermodynamics of multi-component samples.

## II. The Principle

A system is considered which consists of the $N$ components $A_1, A_2, \dots, A_N$. It is employed as an electrode in contact with an auxiliary electrolyte which is a conductor of $A_k$-ions, as schematically illustrated in Figure 1. A second electrode of defined activity of the component $A_k$ is used at the other side of the cell for reference and also as an ionic source or sink. The activity of $A_k$ in this reference electrode should not change with the removal or addition of this component. Possibilities are the use of the pure material $A_k$ or a 2-phase mixture in a 2-component system which includes $A_k$. If necessary, separate potential (reference) and current (counter) electrodes may be used.

By permitting or forcing a current to pass through the electrical circuit, $A_k$ ions are carried across the electrolyte from the right hand electrode to the sample, where the ionic current is converted into an electronic current. By inverting the direction of the current, species $A_k$ may also be removed from the sample. If the transference number of the $A_k$ ions in the electrolyte is unity, the time integral of the current $\int I\,dt$ is a precise measure of the change in the content of $A_k$. If $z_k$ is the charge number of $A_k$, the change in the mass of the sample is

$$|\Delta m| = (M_{A_k}/|z_k|F)\int I\,\mathrm{d}t\,. \qquad (1)$$

$M_{A_k}$ and $F$ are the atomic weight of $A_k$ and Faraday's constant, respectively. The charge flux through the cell, $\int I\,\mathrm{d}t$, may be determined by a coulometer, or it is often simpler to use a constant current for a fixed period of time. The resolution in measuring mass changes in this manner is extremely high compared to the use of typical mass balances. 1 Asec corresponds to $10^{-5} \cdot M_{A_k}/|z_k|$ grams, and considerably less than $10^{-5}$ Asec is still measurable. In the case of oxygen, such a charge corresponds to $8 \times 10^{-10}$ g.

The concentration of component $A_k$ may be varied between essentially zero to practically 100% of the sample. The concentrations of the other species are determined by the preparation of the sample. The number of samples which have to be prepared for phase diagram determinations using this technique is reduced by approximately an order of magnitude compared to those needed for conventional annealing experiments. For studying $N$-component systems, only as many samples are necessary as conventionally used to study an $(N\text{-}1)$-component system. In addition, the problem of the unavoidable lack in precision in preparing samples of defined compositions only appears in the electrochemical technique with the starting compositions, as all subsequent changes can be precisely measured. In the case of ternary systems (components $A_1$, $A_2$ and $A_3$, $N=3$), the attainable compositions are located on straight lines in the equilateral Gibbs triangle which connect the corner of the pure electroactive component and the composition determined by the other components on the opposite side of the triangle. This is illustrated in Fig. 2 by dotted lines for three samples. $A_1$ is the electroactive component and 1-phase regions are indicated by dotted areas while 2-phase regions are shaded.

On the other hand, the cell voltage $E$ is a measure of the activity $a_{A_k}$ of the neutral electroactive component $A_k$ according to Nernst's equation

$$E = \frac{kT}{z_k q} \ln \frac{a_{A_k}\,(\text{sample})}{a_{A_k}\,(\text{reference electrode})}\,; \tag{2}$$

$k$, $T$ and $q$ are Boltzmann's constant, the absolute temperature and the elementary charge, respectively.

The Stockholm convention [43] regarding signs is employed here, i. e. the cell voltage is positive if the right hand side electrode is positive and a current is positive if positive charges are transported to the right or negative ones to the left.

The cell voltage which is observed after the sample comes to equilibrium may also be related to the change of the Gibbs (free) energy $\Delta G$ accompanying the addition or removal of species $A_k$ according to the law of conservation of energy. If $\delta A_k$-ions are added to the sample, this relation is given by

$$E = \frac{\Delta G}{z_k\, q\, \delta}, \tag{3}$$

if $\Delta G$ is related to one formula unit.

According to Gibbs' phase rule, the activities of all components are independent of the composition as long as (the same) $N$ phases co-exist at fixed temperature and pressure, i. e. the same cell voltage is observed regardless of how much $A_k$ has been titrated into or out of the sample. In contrast, the voltage changes with the composition as soon as the composition changes such that a smaller number of phases is present under equilibrium conditions. In this way, the usually large $N$-phase regions are recognizable by a constant value of the cell voltage over a range of compositions. That is illustrated in Fig. 3 for the case of titration along the left hand tie-line of the hypothetical ternary system shown in Figure 2. The voltage observed in equilibrium after each titration step is plotted versus the atomic percentage of the electroactive component $A_1$ at the fixed atomic ratio $A_2/A_3$, which is related to the charge $\int I\,dt$ passed through the cell. The ranges of the 3-phase regions are simply detected from the lengths and locations of the voltage plateaus.

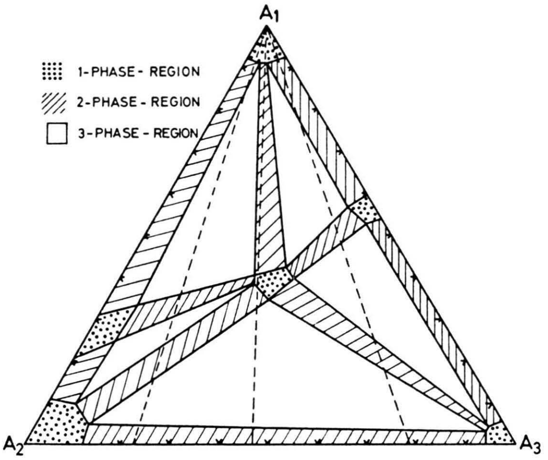

Fig. 2. Hypothetical ternary phase diagram (Gibbs triangle) of the components $A_1$, $A_2$ and $A_3$. $A_1$ is the electroactive component. 1-, 2- and 3-phase regions are differently marked. The dotted lines indicate the accessible compositions for three samples with different $A_2/A_3$ ratios.

## III. Titration Considerations

Atomic percentages of the components are usually plotted in phase diagrams. The charge passed through the galvanic cell is, however, not linearly related to the change in the atomic percentage of the electroactive component, but has to be larger the greater the species $A_k$ concentration is already present in the sample. This relationship is easily derived from considering Faraday's law.

If a sample with the starting composition (integrated over all phases)

$$A_{1_{x_1}} A_{2_{x_2}} \ldots A_{N_{x_N}}$$

and the mass $m$ is considered, the atomic percentage $y$ of the component $A_k$ is given by

$$y = 100\, x_k / \sum_{i=1}^{N} x_i \,. \tag{4}$$

Therefore, the change of $x_k$ with the percentage of $A_k$ is

$$\frac{\mathrm{d}x_k}{\mathrm{d}y} = \frac{100 \sum\limits_{i=1,\neq k}^{N} x_i}{(100-y)^2} \,. \tag{5}$$

In order to obtain the charge $Q = \int I\,\mathrm{d}t$ which is necessary to change the content of $A_k$ by 1%, (5) has to be multiplied by the total charge of species $A_k$,

$$Q(\Delta A_k = 1\%) = \frac{100\,|z_k|\,F\,m \sum\limits_{i=1,\neq k}^{N} x_i}{(100-y)^2 \sum\limits_{i=1}^{N} x_i M_{Ai}} \,. \tag{6}$$

$M_{Ai}$ is the atomic weight of species $A_i$. Integration of (6) yields the charge necessary to change the composition of $A_k$ from $y_1$ to $y_2$ atomic percent:

$$Q(y_1 \rightarrow y_2\,\%\,A_k) = \frac{100\,|z_k|\,F\,m\,|y_2 - y_1| \sum\limits_{i=1,\neq k}^{N} x_i}{(100-y_2)\,(100-y_1) \sum\limits_{i=1}^{N} x_i M_{Ai}} \,. \tag{7}$$

The apparent complexity of this equation has no basic physical origin, but is merely due to the custom of plotting phase diagrams directly in percentages.

## IV. Cell Voltage Considerations

As mentioned before, the equilibrium cell voltage is independent of composition within $N$-phase regions of any $N$-component system. It is determined by the Gibbs energies of formation $\Delta G_f{}^0$ of the $N$ co-existing compounds with the stoichiometric formulas

$$A_{1_{x_{2i}}}\, A_{2_{x_{2i}}} \ldots A_{N_{x_{Ni}}} \quad i = 1, \ldots, N \,.$$

The number of molecules of each compound $i$ is described by $n_i$. For simplicity it is assumed that the reference electrode has an activity of the electroactive component $A_k$ equal to 1. If that is not the case, the voltage of a hypothetical galvanic cell with the electrode actually used and one of activity 1 has simply to be added to the measured cell voltage. As in Fig. 1, the sample is assumed to be the left hand side electrode.

We now consider the virtual coulometric titration of $\delta$ ions $A_k$ with the charge number $z_k$ into the sample, which is assumed to still remain in the $N$-phase region. The cell reaction may be written

$$\sum_{i=1}^{N} n_i\, A_{1_{x_{1i}}}\, A_{2_{x_{2i}}} \ldots A_{N_{x_{Ni}}} + \delta A_k = \sum_{i=1}^{N} n_i{}'\, A_{1_{x_{1i}}}\, A_{2_{x_{2i}}} \ldots A_{N_{x_{Ni}}} \,, \tag{8}$$

where the new number of molecules is reflected by $n_i{}'$. The change of the Gibbs energy according to this reaction, $\Delta G$, is related to the cell voltage by (3). As is seen from (8), $\Delta G$ may be composed of the Gibbs energies of formation of the individual $N$ compounds by

$$\Delta G = \sum_{i=1}^{N} (n_i{}' - n_i)\, \Delta G_f{}^0 (A_{1_{x_{1i}}}\, A_{2_{x_{2i}}} \ldots A_{N_{x_{Ni}}}) \,. \tag{9}$$

In order to determine the factors $(n_i{}' - n_i)$, the following conditions have to be fulfilled because of the requirement for the conservation of the atomic species

$$\begin{aligned}
&\sum_{i=1}^{N} (n_i{}' - n_i)\, x_{1i} = 0 \,, \\
&\quad\vdots \\
&\sum_{i=1}^{N} (n_i{}' - n_i)\, x_{(k-1)i} = 0 \,, \\
&\sum_{i=1}^{N} (n_i{}' - n_i)\, x_{ki} = \delta \,, \\
&\sum_{i=1}^{N} (n_i{}' - n_i)\, x_{(k+1)i} = 0 \,, \\
&\quad\vdots \\
&\sum_{i=1}^{N} (n_i{}' - n_i)\, x_{Ni} = 0 \,,
\end{aligned} \tag{10}$$

This is a system of $N$ equations for the $N$ unknowns $(n_i{}' - n_i)$ and may be solved according to Kramer's rule:

$$(n_i{}' - n_i) = (d_i / d) \tag{11}$$

where $d$ is the determinant formed by the coefficients of $(n_i{}' - n_i)$:

$$d = \begin{vmatrix} x_{11}\; x_{21} & \ldots & x_{N1} \\ x_{12}\; x_{22} & & \\ \vdots & & \\ x_{1N}\; x_{2N} & \ldots & x_{NN} \end{vmatrix} \tag{12}$$

and $d_i$ is the determinant $d$ in which the $i$-th line is replaced by the values on the right hand side of the equality signs of the system of Eq. (10)

$$d_i = \begin{vmatrix} x_{11} & x_{21} & \dots x_{k1} & \dots x_{N1} \\ \vdots & & & \\ x_{1(i-1)} & x_{2(i-1)} & \dots x_{k(i-1)} & \dots x_{N(i-1)} \\ 0 & 0 & \delta & 0 \\ \vdots & & & \\ x_{1N} & x_{2N} & \dots x_{kN} & \dots x_{NN} \end{vmatrix} \qquad (13)$$

The determinant $d_i$ may be expressed by the minor $d_{ik}$, which is the determinant formed by eliminating the $i$-th line and $k$-th row of the determinant $d$, in the following way

$$d_i = (-1)^{i+k}\,\delta d_{ik}\,. \qquad (14)$$

The Gibbs reaction energy $\Delta G$ is then given by

$$\Delta G = \frac{\delta}{d}\sum_{i=1}^{N}(-1)^{i+k}\,d_{ik} \cdot \Delta G_f^0(A_{1_{x_{1i}}}A_{2_{x_{2i}}}\dots A_{N_{x_{Ni}}})\,. \qquad (15)$$

This yields for the cell voltage according to (3)

$$E = \frac{(-1)^k}{z_k\,q\,d}\sum_{i=1}^{N}(-1)^i\,d_{ik} \cdot \Delta G_f^0(A_{1_{x_{1i}}}A_{2_{x_{2i}}}\dots A_{N_{x_{Ni}}})\,. \qquad (16)$$

The $N$ compounds may be listed from 1 to $N$ in any sequence. (16) may be conveniently applied to systems of any number of components $N$. It only involves the Gibbs energies of formation of the phases present and virtual reactions no longer have to be considered. The formula is therefore also of advantage even for binary systems.

If an $N$-phase region is composed of ($N$-1) phases which consist of the same ($N$-1) components (the electroactive component $A_k$ must be included), the Gibbs energy of formation of the remaining $N$-th phase does not contribute to the cell voltage. That means in the case of ternary systems that the voltages in 3-phase regions which have one side in common with either one of the two legs of the Gibbs triangle which contain the electroactive component, are determined by the two binary phases, independent of the composition of the third phase.

With the knowledge of the observed equilibrium o. c. cell voltages of the $N$-phase regions, (16) allows the determination of the Gibbs energies of all the compounds existing in the system. However, when several $N$-phase regions have to be taken into consideration for the determination of a certain $\Delta G_f^0$ value, it is necessary to assume that the stoichiometric ranges are small enough to consider the same composition to be present in adjacent $N$-phase regions. The entropies of formation, $\Delta S_f^0$, may be obtained from the temperature dependence of the $N$-phase region o. c. voltages:

$$\frac{\partial E}{\partial T} = \frac{(-1)^{k+1}}{z_k\,q\,d}\sum_{i=1}^{N}(-1)^i\,d_{ik} \cdot \Delta S_f^0(A_{1_{x_{1i}}}A_{2_{x_{2i}}}\dots A_{N_{x_{Ni}}})\,, \qquad (17)$$

assuming that no changes in the stoichiometric numbers of the compounds appear with the variation of the temperature. If that assumption does not hold, the determinants $d$ and $d_{ik}$ also have to be differentiated. The enthalpies of formation, $\Delta H_f^0$, of all compounds can readily be found from making use of the thermodynamic relation $\Delta H_f^0 = \Delta G_f^0 + T\,\Delta S_f^0$.

In addition to the previously described procedure for the determination of thermodynamic data, such data may also be obtained in a different way from electrochemical titration measurements. The data may even be derived as functions of the stoichiometry of the compounds. This method is applicable both for narrow and wide range phases. Beside obtaining more detailed thermodynamic information, it also overcomes the problems that might arise when quite different stoichiometries of a compound are in equilibrium in different $N$-phase regions, as mentioned above.

The reaction equation for changing the concentration of species $A_k$ by the amount $\delta$ may be written as

$$A_{1_{x_1}}A_{2_{x_2}}\dots A_{k_{x_k}}\dots A_{N_{x_N}} + \delta A_k = A_{1_{x_1}}A_{2_{x_2}}\dots A_{k_{x_k+\delta}}\dots A_{N_{x_N}}\,. \qquad (18)$$

This reaction may refer to either a change in the stoichiometry of a single phase in a 1-phase region or in the relative amounts and compositions of the phases if any arbitrary number of phases from 2 to $N$ is present. The cell voltage is again related by (3) to the $\Delta G$-value accompanying reaction (18) which may be also considered as the formation of

$$A_{1_{x_1}}A_{2_{x_2}}\dots A_{k_{x_k+\delta}}\dots A_{N_{x_N}}$$

and the decomposition of

$$A_{1_{x_1}}A_{2_{x_2}}\dots A_{k_{x_k}}\dots A_{N_{x_N}}\,.$$

In terms of Gibbs formation energies we have therefore, considering infinitesimal changes,

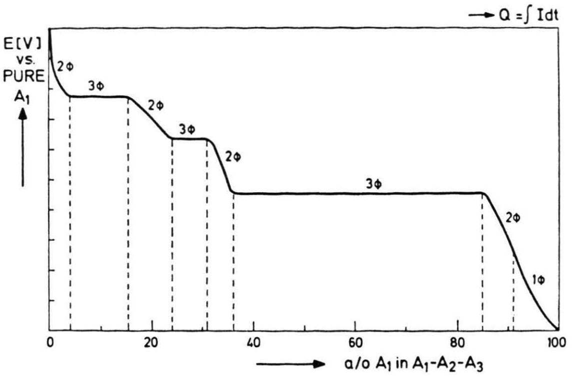

Fig. 3. Equilibrium cell voltage versus the atomic percentage of $A_1$ for an electrochemical titration along the tie-line on the left hand side of the ternary phase diagram shown in Fig. 2. 3-phase regions are recognized by voltage plateaus, whereas 1- and 2-phase regions show changes of the cell voltage with the composition.

$$E = \frac{1}{z_k\, q} \frac{d[\Delta G_f^0(A_{1_{x_1}} A_{2_{x_2}} \dots A_{k_{x_k}} \dots A_{N_{x_N}})]}{d\, x_k} \,. \qquad (19)$$

The integration of this equation yields for the Gibbs energy of formation as a function of the composition within any region

$$\begin{aligned} \Delta G_f^0(A_{1_{x_1}} A_{2_{x_2}} \dots A_{k_{x_k}} \dots A_{N_{x_N}}) \\ = z_k\, q \int_{x_{k_0}}^{x_k} E(x_k)\, \mathrm{d}x_k \qquad (20) \\ + \Delta G_f^0(A_{1_{x_1}} A_{2_{x_2}} \dots A_{k_{x_{k_0}}} \dots A_{N_{x_N}}) \,. \end{aligned}$$

The integration has to be carried out along the path of compositions which are accessible by use of the electrochemical titration process. It is related to the area under the coulometric titration curve. If the change of the stoichiometry of species $A_k$ is written in terms of the change of the atomic percentage $y$ of $A_k$ (as plotted in Fig. 3 for the case of a ternary system), one has, according to (5),

$$\begin{aligned} \Delta G_f^0(A_{1_{x_1}} A_{2_{x_2}} \dots A_{k_{x_k}} \dots A_{N_{x_N}}) \\ = 100 z_k\, q \left( \sum_{i=1, \neq k}^{N} x_i \right) \int_{x_{k_0}}^{x_k} E(y)/(100-y)^2\, \mathrm{d}y \qquad (21) \\ + \Delta G_f^0(A_{1_{x_1}} A_{2_{x_2}} \dots A_{k_{x_{k_0}}} \dots A_{N_{x_N}}) \,. \end{aligned}$$

Any value of $x_{k0}$ may be used in the integration constant

$$\Delta G_f^0(A_{1_{x_1}} A_{2_{x_2}} \dots A_{k_{x_{k_0}}} \dots A_{N_{x_N}}) \,,$$

particularly $x_{k0} = 0$ when it is the Gibbs energy of reaction mixing all other components but the electroactive one. The resolution in determining $\Delta G_f^0$ is very high since voltages and currents may be measured very precisely. The temperature dependence of $\Delta G_f^0$ at fixed composition yields the entropy and enthalpy of formation in the well known way as described above. (20) or (21) may be applied in order to determine the Gibbs energies of formation of all existing phases as well as their relative variation with stoichiometry.

## V. Experimental Example

The electrochemical titration technique has been applied to study the phase diagram and the thermodynamics of the ternary system Cu – Ge – O. Yttria or calcia stabilized zirconia was used as the solid electrolyte for the transport of oxygen ions. 2-phase mixtures of Cu and $Cu_2O$ or air of atmospheric pressure served as ionic sources or sinks and as oxygen reference electrodes. The results of titrations at 900 °C along several lines of equal Cu : Ge ratios (4 : 1, 3 : 2, 1 : 1 and 1 : 3) within the triangle CuO – Cu – $GeO_2$ are shown in Figure 4. Identical symbols represent the same cell voltages and therefore 3-phase regions. Their boundaries are readily constructed by connecting the edges of the observed voltage transitions by straight lines. In the present case, the extents of the 1- and 2-phase regions (beside the Cu(α)-phase) were found to be very small compared to those of the 3-phase areas. The copper metagermanate $CuGeO_3$ is the only ternary com-

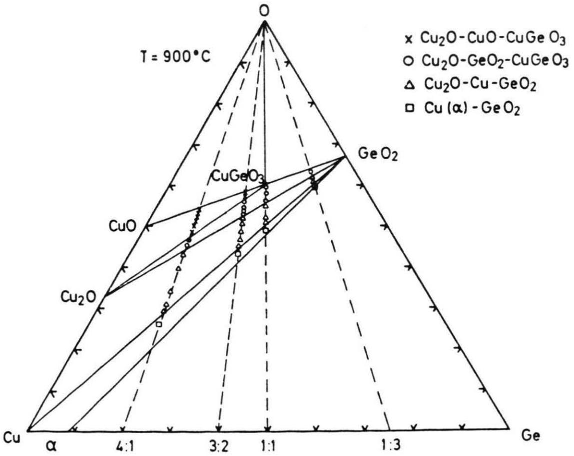

Fig. 4. Representation of the phase diagram obtained for the ternary system Cu–Ge–O by electrochemical titration with the help of a solid zirconia oxygen ion conductor. The various symbols indicate regions of equal voltages. 2-phase regions border each of these areas.

pound in the system which exists in the temperature range investigated: 750 – 950 °C. It is in thermodynamic equilibrium with CuO, $Cu_2O$, $GeO_2$ and pure oxygen.

The Gibbs energy of formation of $CuGeO_3$ may be derived from the cell voltage in the 3-phase region $Cu_2O - CuGeO_3 - GeO_2$ according to (16). The $\Delta G$-values of the binary oxides are found from the voltages of the 3-phase regions which have one side in common with the legs of the Gibbs triangle. The integrational contributions according to (20) or (21) in the present case are negligibly small due to the narrow ranges of existence of the compounds. From the experimental results, the standard Gibbs energy of formation of $CuGeO_3$ was found to be

$$\Delta G_f^0(\mathrm{CuGeO_3}) = (-756.3 + 0.284\,\mathrm{T})\,\mathrm{kJ/mol} \quad (1073 \leqq T[\mathrm{K}] \leqq 1223)\,.$$

The specific experimental details and a full presentation and analysis of the experimental data are given elsewhere [44].

## VI. Discussion

Compared to other techniques for determining phase diagrams and thermodynamic data, the following general advantages of the described electrochemical technique may be realized:

- Both phase diagram and thermodynamic information are available from the same experiment. The importance of this fact is not only an increased knowledge of the system, but there is a mutual influence in understanding and in the confidence of the results.
- The technique is experimentally very tractable. Both the experimental set-up is usually uncomplicated and the performance of the experiments involves only the control or measurement of readily and precisely accessible electrical quantities. Only a comparatively small number of specimens has to be prepared. The main limitation is seen in the availability of proper electrolytes.
- The data are obtained in situ. No quenching of the sample, with possible phase or composition changes, and thus potentially erroneous interpretations, is necessary.
- The resolution is extremely high due to the fact that the measurements of mass changes are reduced to the determination of electrical charges. In this way, even narrow existence ranges become readily accessible.

In conclusion, the described electrochemical method should be considered as a very powerful and elegant technique for investigating phase diagrams and thermodynamic data of systems with an arbitrary number of components.

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