COMPUTATION OF LIQUIDUS RELATIONSHIPS IN MULTICOMPONENT BINARY SALT SYSTEMS

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ABSTRACT

An empirical relationship between temperature and composition of a liquid phase at equilibrium with a crystal phase is derived from the ideal by replacing the heat of melting with a polynomial expression of second order in terms of the concentration of foreign components in the liquid. Functions of this form describe very well the available experimental data on alkali halide systems. Practical procedures for calculating required parameters, and their use in computing eutectic points and liquidus surfaces in multicomponent binary salt systems with any combination of common cations and anions of any valency are described briefly. FORTRAN II programs for a 7090 computer, based on these algorithms, have been written and tested.

INTRODUCTION

Complex salt systems are receiving increasing attention from geochemists interested in systems which model igneous and metamorphic rocks at temperatures at or near the liquidus. In addition, many minerals can be recrystallized in salt melts but there is little available information on eutectic compositions and temperatures in multicomponent systems. The many variables of such systems make graphical analysis clumsy and computational methods are tedious. The advent of fast computers and subject-oriented programming languages such as FORTRAN has obviated these difficulties and made it practical to calculate liquidus relationships in salt systems of any complexity.

In this discussion we restrict the complexity to binary salt components which do not form double salts. In the computer programmes, the number of different cations, also anions, is limited to 6, giving a limit of 36 different salts with a corresponding number of liquidus hyper-volumes, and over 4 million 11-fold eutectics. These limits, however, can be increased indefinitely by a change in dimension declarations.

EMPIRICAL LIQUIDUS FUNCTION

Under conditions of thermodynamic equilibrium in a heterogeneous system consisting of a crystalline phase and a liquid phase,

$$\ln\left(\frac{a_l}{a_c}\right) = \frac{-\Delta H_s}{RT} + \frac{\Delta S_s}{R}$$

where a_l and a_c (the activity of the principal or solvent component in liquid and solid solution) and also ΔH_s and ΔS_s (the differential heat and entropy of solution) are functions of temperature, pressure, and total composition. The forms of such functions are complex, mostly imperfectly established as to generality, and usually depend on some empirical function. A logical procedure is to simplify the form of the basic function and make its parameters depend directly on experimental measurements.

We can simplify by taking activities as being proportional to composition, and also by combining any departure of a_c from unity along with variations of ΔH_s and ΔS_s from constancy, giving the approximation

$$\ln C_l \approx \frac{-h}{T} + s$$

where h and s are constants. Since ΔH_s and ΔS_s are constant as a first approximation, and at the melting temperature of the pure solvent,

$$\Delta S_s = \frac{\Delta H_s}{T_m},$$

then

$$s \approx \frac{h}{T_m},$$

and

$$\ln C \approx h\left(\frac{1}{T_m} - \frac{1}{T}\right).$$

In this approximate equality, C is the mole fraction of principal component (or solvent) in the liquid phase at equilibrium with the crystal phase, h is a constant dependent on the kind (or kinds) of minor component(s) present, T_m is the melting temperature of the pure solvent, and T is the temperature of the equilibrium, both temperatures being in degrees Kelvin.

Liquidus functions of the above type, with one parameter (other than T_m) describe many experimental liquidus curves fairly closely. Liquidus curves of some compounds of the double salt type are significant exceptions, but we are excluding them from the argument.

Usually there is a significant improvement of the fit of the liquidus function if the parameter h is replaced by an expression in terms of the mole fraction of solute in the liquid phase. Choosing a polynomial expression for computational simplicity, the liquidus function becomes

$$\ln C = (h_0 + h_1(1 - C) + h_2(1 - C)^2 + \ldots)(1/T_m - 1/T).$$

A survey of experimental data on alkali halide binary systems along with a series of computations indicated that the slope expression need be no more than of second order for the liquidus function to be well within the experimental precision. Consequently, second order polynomial slope expressions are used in the following programmes. For some purposes a first order polynomial is adequate, but if the experimental data are exceptionally precise a third order polynomial may be desirable. Changes of this kind can be made in the following programmes by an alteration of relatively few statements, declarations, and specifications.

The effective concentration of an ionized binary salt in solution varies as the product of the concentration of its constituent ions. Assuming that the effects of cation and anion additives are independent and can be combined linearly, the net slope expression is the reciprocal of the sum of the linearly weighted reciprocals of the two slope expressions, and the liquidus function can be written as

$$\ln(x \times y) = f(x, y)(1/T_m - 1/T),$$

where

$$f(x, y) = 1\Big/\left[\left(\frac{1-x}{2-x-y}\right)\Big/(a + b(1-x) + c(1-x)^2) + \left(\frac{1-y}{2-x-y}\right)\Big/(p + q(1-y) + r(1-y)^2)\right],$$

x and y are the concentrations of X and Y in the liquid phase at equilibrium with the salt XY, a, b, and c are the mean parameters for cation additives and p, q, and r are the mean parameters for anion additives.

We calculate the mean slope polynomial for cation additives by a combination in the following way:

$$a + b(1-x) + c(1-x)^2 = 1\Big/\sum_{\substack{k=1\\k\neq i}}^{n_c} (g_k/(a_{i,j,k} + b_{i,j,k}h_k + c_{i,j,k}h_k^2)),$$

where ($k = 1, n_c$) are the indices of the cations in the system, i and j are the respective indices of the cation and anion of the crystal phase, and

$$g_k = x_k/(1 - x_i),$$
$$h_k = g_k^v(1 - x_i) + (1 - g_k^v)x_k,$$

where v is a data constant which is set at some positive value for any one computation but can be treated as a variable between computations. The polynomial for anion additives is obtained by an analogous summation.

In the computer programmes, the combination of the two mean polynomials is done in subroutine (AVPARC) which has i and j as input arguments and a single output which we can call $f_{i,j}$. Thus the liquidus function can be written in the following simple form:

$$\ln(x_i \times y_j) = f_{i,j}\left(\frac{1}{(T_m)_{i,j}} - \frac{1}{T}\right).$$

(The matrix of slope function parameters is read in by the main programme which stores it as a global constant so that it does not have to be transmitted to the subroutine each time it is called. All other constants required by AVPARC are stored in the same way, leaving only the indices, i and j, as its variable input arguments.)

CALCULATION OF THE SLOPE PARAMETERS

The slope parameters (a, b, c, p, q, r) are calculated by a separate programme (LIQPAR), from liquidus data of binary systems in which there is either a common cation or common anion. For example, data on the system LiCl—KCl would allow calculation of two sets of a, b, and c parameters and analogously the system LiCl—LiI would allow calculation of two sets of p, q, and r parameters.

In any one system the temperature—composition data are set into three groups, more or less equally spaced between the pure solvent and the composition of the eutectic. The programme averages each group after transforming mole fractions of solvent to logarithms and temperatures to reciprocals of absolute temperature. The three means of the transformed data are changed back to mole fractions and absolute temperature and the parameters are calculated by usual methods of linear algebra.

The problem of multiple valency of components is solved simply by considering each to have unit valence. For example, experimental data for the liquidus of $CaCl_2$ in the system $CaCl_2$—LiCl are a recast by the programme to mole fractions of $Ca_{0.5}Cl$ in the system $Ca_{0.5}Cl$—LiCl before the slope parameters are calculated from the three mean data points. This convention of unit valence molarity simplifies the calculation of multicomponent liquidus relationships by eliminating the large possible number of combinations of multiple valency in the anions or cations of the constituent salts.

There is some practical advantage in having LIQPAR as a separate programme rather than as a subroutine since the output parameters can be punched on cards and marked with the appropriate solvent and solute salt names. These can be filed alphabetically and then combined in various ways for other programmes which require the same slope parameters. To facilitate error-checking, indexing of these parameter cards should agree in sense with the (i, j, k) numerical indexing in programmes which read them. For example the punched card with a, b, and c parameters for LiCl in the system LiCl—KCl should be labelled "Li, Cl, K," and the p, q, and r parameters for LiCl in the system LiCl—LiI should be labelled "Li, Cl, I."

CALCULATION OF MULTIPHASE EUTECTICS

In multicomponent binary salt systems the number of independent components is one less than the sum of the number of cations and anions, there being one restriction that ionic charges balance. If temperature is the only other variable, then the highest order of eutectics, i.e., the largest number of crystalline phases at an invariant eutectic point also is $(n_c + n_a - 1)$. Since the number of possible crystal phases is $(n_c \times n_a)$, the number of eutectic points is the combinations of $(n_c \times n_a)$ things taken $(n_c + n_a - 1)$ at a time, less the number of combinations which do not include all of the cations and anions. Among the possible eutectics, many are metastable in the sense that at the intersection of a set of $(n_c + n_a - 1)$ liquidus surfaces (or volumes, etc.), at least one other liquidus exists at a higher temperature at that composition. The scheme of computation described below consists of calculating the composition and temperature of all possible eutectics in a multicomponent system and examining each to determine whether any other liquidus is at a higher temperature. In the programme called LIQEUS, the temperature and composition values of each eutectic are printed, and then labelled if metastable.

The slope parameters are those for the unit valence salts as discussed above, but the actual valencies are read in with the data and used to convert the compositional results into mole fractions of the conventional formulations at the end of the programme.

Since each liquidus intersects the others of any one set of salts, we start by eliminating T. Rearranging any one equation,

$$T = \frac{(T_m)_{i,j} \times f_{i,j}}{f_{i,j} - (T_m)_{i,j} \times \ln(x_i y_j)},$$

and equating any two such equations and rearranging,

$$x_i y_j = \exp\left(f_{i,j}\left(\left(\frac{1}{(T_m)_{i,j}} - \frac{1}{(T_m)_{ip,jp}}\right) + \frac{\ln(x_{ip} y_{jp})}{f_{ip,jp}}\right)\right).$$

Direct solution is impossible since the form of the equation is

$$x_i \times y_j = w_{i,j} = \text{function } (x_i, y_j, \text{etc.}),$$

but there is a fairly rapid convergence in a Seidel type of iteration. If indices j and jp are the same number,

$$x_i = w_{i,j}/y_j,$$

and if i and ip are the same number,

$$y_j = w_{i,j}/x_i.$$

However, if we carry out the iterative calculation by using

$$(x_i)_{n+1} = \text{function } ((x_i)_n, y_j, \text{etc.})$$

or

$$(y_j)_{n+1} = \text{function } (x_i, (y_j)_n, \text{etc.})$$

the convergence is oscillatory and tends to be slow. This is changed to a monotonic and faster convergence by damping each change as follows:

$$(x_i)_{n+1} = (x_i)_n + ((x_i)_{n+1} - (x_i)_n)/n_c,$$

$$(y_j)_{n+1} = (y_j)_n + ((y_j)_{n+1} - (y_j)_n)/n_a.$$

When indices i and ip are different and also j and jp are different, then x_i and y_j are changed in each cycle as follows:

$$(x_i)_{n+1} = (x_i)_n + (d_{i,j})_{n+1}/n_c,$$

$$(y_j)_{n+1} = (y_j)_n + (d_{i,j})_{n+1}/n_a,$$

where

$$(d_{i,j})_{n+1} = \frac{(x_i y_j)_{n+1} - (x_i y_j)_n}{(x_i)_n + (y_j)_n}.$$

After each segment of the cycle, that is, after x_i or y_j or both x_i and y_j are changed, all cation and anion concentrations are normalized so that

$$\sum_{k=1}^{n_c} x_k = \sum_{k=1}^{n_a} y_k = 1.$$

The starting values of the cation and anion mole fractions are those computed at the midpoint composition of the set of m salts. Each iteration per pair of liquidus intersections gives one additional digit of precision. In the programme LIQEUS there are ($10 \times m$) iterations, giving at least 8-digit precision.

CALCULATION OF TERNARY LIQUIDUS SURFACES

For some purposes, more information on liquidus curves, surfaces, volumes, etc. may be needed after the stable eutectics are calculated by LIQEUS. Computation of the temperature at 55 points on a regular triangular network on each of the three liquidus surfaces of a given ternary system can be done according to the programme LIQTEM.

The method consists simply of selecting compositional points at 0.1 mole fraction intervals and directly calculating temperatures using the reciprocal form of the liquidus function:

$$T = (T_m)_{i,j}/(1 - ((T_m)_{i,j}/f_{i,j}) \ln (x_i \times y_j)).$$

After each temperature is calculated, the total composition is recast to units of mole fraction of the salt components in their usual formulations.

If there are experimental data for any of the liquidus surfaces, the user has the option of varying the exponent of the weighting constant (i.e., by varying the input value of CON used by subprogramme AVPARC) and selecting the value that gives the best fit to the liquidus data. The calculated liquidus surfaces are not sensitive to variation of CON, but preliminary tests of LIQTEM indicate that in ternary alkali halide systems with a common anion its best value probably is near unity.

THE FORTRAN COMPUTATION PROGRAMMES

The parameter-calculating programme LIQPAR reads in valency constants and experimental liquidus data for one side of a binary system, in units of mole fraction of solvent and degrees C, and outputs the three unit-valency parameters for the slope function discussed above.

The eutectic-calculating programme LIQEUS reads in several control constants and matrix of slope parameters and, with the help of subprogramme AVPARC, computes the composition and temperature of the highest order eutectics in the given system. The output values are marked if the eutectic is metastable.

The temperature-calculating programme LIQTEM reads in matrix of slope parameters for a selected ternary system and computes the temperatures at 55 regularly spaced compositional points on each of the three liquidus surfaces. It uses subprogramme AVPARC, which is the same as above except for reduced dimensions of the arrays.

The execution time for any of the above programmes operating on data of ternary systems is about one second.

Copies of programmes LIQPAR, LIQEUS, AVPARC, and LIQTEM, in the form of punched card decks of column-binary instructions for an IBM 7090 computer under monitor control are avaliable, also punched card decks of the FORTRAN statements.

APPLICATION OF THE PROGRAMMES TO REAL SYSTEMS

A study is currently being made of the utility of the above programmes in investigations of ternary systems of binary salts. Preliminary results using published data indicate that probably there is no large error of logic in the programmes but we have not determined quantitatively the error of fit of calculated ternary liquidus surfaces to measurements. However, the results indicate that the above programmes can be used at least as approximate predictors of ternary melting relationships from binary information. Accordingly, a relatively small number of measurements of ternary liquidus temperatures acting as correctors of the predictors, may suffice for an adequate definition of the desired temperature-composition relationships.

We plan to use the above programmes to compute the liquidus of multicomponent systems which include calcite and/or dolomite because of the current interest in hypotheses about carbonatite magmas. The effect of a large number of relatively minor components on the liquidus of the major mineral component or components can be computed easily by these methods.

Application of the above computer programmes to silicate systems is not so simple because (1) an assumption that each binary oxide component is ideally ionic may be grossly in error, and (2) many of the liquidus relationships of interest are of binary, ternary, or higher order compound oxides. A study is being made of a revision of the above logic, starting with an assumption of molecular species of the minerals in the liquid state. The results of this will be published in the near future.

ACKNOWLEDGEMENTS

Officers of the Institute of Computer Science of the University of Toronto were helpful in providing computer facilities and advice. Mr. J. Wells assisted by indexing the published liquidus data on alkali halide systems.

Manuscript received May 20, 1964