MACHINE PLOTTING OF LIQUIDUS DATA OF BINARY AND TERNARY SALT SYSTEMS

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ABSTRACT

Programmes for machine plotting of computed liquidus curves of binary salt systems and liquidus isotherms of simple and reciprocal ternary salt systems have been coded in FORTRAN IV for an IBM 7094 computer and a CALCOMP plotter.

INTRODUCTION

This is a report of progress in developing practical procedures for computing and plotting liquidus phase boundaries in systems of mineralogical interest.

Previous papers (Smith, 1964, 1965, 1966) outlined generalizations and simplifications adopted for salt systems and for silicate systems. In essence it is assumed that salt systems are ideally ionic and silicate systems are ideally molecular. Although both assumptions are false, the computing methods use experimental liquidus data of real binary systems to predict relationships in systems of higher order. Thus errors committed in adopting simplifying procedures are compensated to some degree by using the same procedures in opposite sense to generate extrapolations and combinations. However, the method does not provide for large departures of properties of the liquid phase from those of an ideal solution, and specifically does not predict liquid immiscibility and formation of complexes.

COMPUTATION AND PLOTTING OF LIQUIDUS PHASE BOUNDARIES

Isobaric liquidus boundaries in binary salt systems are assumed to be describable by the following functional relationship:

$$\ln x = (a + b(1 - x) + c(1 - x)^2)(1/Tm - 1/T)$$

where x is the ionic fraction of the unique cation or anion characterizing the crystal phase, a, b, and c are unit valence parameters computed from experimental data, and Tm is the melting temperature of the pure crystal phase.

The unit valence parameters are computed by a programme (LIQPAR) that recasts the compositional data to ionic fractions of fictive unit valent species before evaluating a, b, and c for least square fit. For example, in the system $LiF—CaF_2$, if a compositional point is at 0.5 LiF, then the cation fraction is 0.5 Li but the unit valent cation fraction is 0.333 Li. This distorts the data, but in using the parameters to compute the liquidus, the unit valent ionic fractions normally are transformed back to refer to the usual formulations. In addition to simplifying the programming, this scheme allows direct computation of liquidus curves for combinations such as $Li_2F_2—CaF_2$ (termed by Russian investigators the equivalent formulations) by using the unit valent parameters and not recasting to the normal formulations, $LiF—CaF_2$.

After the unit valent parameters are computed, the function is used in reverse sense to generate a list of liquidus temperatures for regular increments of additive salt. The temperatures and compositions are transformed to appropriate values in inches for plotting.

Liquidus boundaries in multicomponent salt systems are assumed to be describable by the functional relationship

$$\ln x_i y_j = (a_{ij} + b_{ij}(1 - x_i y_j) + c_{ij}(1 - x_i y_j)^2)(1/Tm_{ij} - 1/T)$$

where x and y are the cation and anion fractions of salt components, i and j are indices referring to the major salt, and a, b, and c are unit valence parameters computed from analogous parameters of all of the component binary liquidus functions. The method of combination of effects of all cation and anion additives is described in detail in a prior paper (Smith, 1965). An adjustable parameter (CON) allows a small arbitrary variability of the effect of more than two cations or two anions. Another adjustable parameter (ARBFAC) has been added to allow a partial correction for the difference in free energy of reciprocal salt pairs, as described below.

For programming convenience, ternary systems are divided into two classes: (1) those with three cations and a common anion, or three anions and a common cation, and (2) those with two cations and two anions. A conventional plotting of compositions is within a triangular plane for the first class and within a square plane for the second class. In higher order systems projections can be made to one or other kind of boundary plane. Algebraically, this consists of keeping the ionic fractions of all but three cations or anions, or two cations and two anions, constant and letting the remainder vary under constraints that the sums of cationic and anionic fractions are each unity and the charges balance. Plotting programmes for both types of ternary systems have been written and tested but ternary projections from systems of higher order have not been attempted.

We use the liquidus function in the form

$$T = f(x_i y_j)$$

to generate a matrix of temperature values for compositional points at intervals of 0.01 ionic fraction of cationic or anionic additives. In this operation we correct for valencies greater than unity if required. If the i-th cation has a valency of n_i and ionic fraction value of x_i, then it has a fictive unit valence ionic fraction of

$$x_i' = n_i x_i / z$$

where

$$z = \Sigma n_i x_i.$$

A similar operation is done on the anions if not all are univalent. In effect, x_i and y_i are the fractional positions for plotting while x_i' and y_i' are the ion fractions used for computing the liquidus temperature.

In an early stage of testing programmes for computing liquidus temperatures in reciprocal salt systems, it became evident that some correction for the stabler diagonal pair of salts would have to be made. No simple way of making this correction without changing the general scheme was devised, but a partial correction with an arbitrary parameter was added. If g_{ij} is the net liquidus slope parameter computed from all the contributors then

$$g_{ij}' = g_{ij}(1 + d(x_1 y_1 x_2 y_2))$$

where d is an arbitrary factor, positive for the two salts on the stable diagonal, and negative for the other two salts. The effect of using g' instead of g to compute liquidus temperatures is to raise the liquidus surfaces of the two salts on the stable diagonal and lower the liquidus surfaces of the other two salts, in the central part of the whole system. The form of this correction has no theoretical justification and its value is not expected to be good if the difference in free energy of the reciprocal pairs of salts is large.

The next step is generation of a temperature value for an isotherm less than the melting temperature of the major salt, and calculation of a set of interpolated compositions for that temperature. The interpolations are made at regular 0.01 ionic fraction intervals of one additive, and the vectors of compositional values are transformed to inches in x and y directions for plotting purposes. Before output of the vectors they are transformed according to which salt of the three (or four) salts the liquidus corresponds.

The sense of transformation of points on isotherms depends on the final arrangement of salts required in the drawing and also on the kind of ternary system. If three salt components have either a common cation or anion but not both, then the drawing is triangular. In this case the first salt is at the lower left corner, the second salt is at the lower right corner and the third salt is at the upper corner. If the ternary system is of reciprocal salt type (with two cations and two anions), the drawing is square. In this case the upper corners are for the salts of the first cation and the left corners are for the salts of the first anion. In all cases the points on the liquidus of any salt are computed as if that salt were at the lower left right-angle corner. Thus for some salts the computed liquidus isotherm points are already in correct sense relative to corners: this is so for the first salt of a simple ternary system and for the salt of the second cation and first anion of a reciprocal ternary system. In other cases appropriate transformations of the computed points are made. These are combinations of simple up—down and right—left reflections and linear shape changes.

We include an optional further transformation of the right triangular arrangement to any shape and size of triangle. This allows a final computation of liquidus points within a conventional equilateral triangle.

The sets of *x*-*y* points on liquidus isotherms are output on tape one after the other, down to a temperature value specified in the data, usually a few degrees lower than the estimated ternary eutectic. The temperature contour interval also is an input data variable.

The next salt component is taken as the major salt and the computations, interpolations and transformations are done in analogous ways. Output of the results causes plotting of three or four sets of isotherms in the triangular or square field.

A separate routine causes output of a set of points in sequence such that the plotter draws a triangle with 0.1 mole fraction divisions, or a square with 0.1 mole fraction marks on the border.

The finished machine drawing does not contain lines representing intersections of the liquidus surfaces, but it is a small matter to mark isothermal intersections and draw smooth curves through them by hand.

A final inked tracing by hand, showing the liquidus surface intersections and only the stable parts of the liquidus surfaces, is normally the final step in the process. This smooths out the 0.01 inch incremental steps that the digital plotting machine draws in approximating curves.

The programmes to carry out the above routines are in FORTRAN IV language for an IBM 7094 computer. The plotting routines are for a CALCOMP digital machine, with eleven-inch width of paper, operated off-line by magnetic tape data written by the computer.

Two programmes were developed for plotting liquidus temperatures as a function of composition in binary systems of salts. Programme LIQBI-M3 causes drawing of the liquidus curve of one salt as a function of concentration of another, either one cation or one anion being common.

This programme is useful for comparing the shape of liquidus curves of one salt with various additives. Programme LIQBI-M4 causes drawing of the liquidus curves of two salts with common cation or anion intersecting at the eutectic point. Since both programmes use liquidus parameters computed for least square deviation from experimental data, the plotted curves are best fit liquidus curves. Both programmes are quite simple and the output plots can be modified readily.

The programme for causing plotting of the liquidus surfaces of a simple ternary system is called LQ3CBS-M5. The order of the salts around the compositional triangle is determined by the sequence of input data presented, and the isothermal intervals on the three liquidus surfaces are set by the input data. In addition, the shape and size of the triangle is specified by factors controlling the length of the base and left-hand sides and by the size of the included angle. As an invariant routine, the programme also causes plotting of compositional lines at 0.1 ion fraction intervals.

The programme for causing plotting of the liquidus surfaces of a ternary reciprocal salt system is called LQDTRS-M5. The order of the salts around the compositional square is determined by the sequence of input data pre-

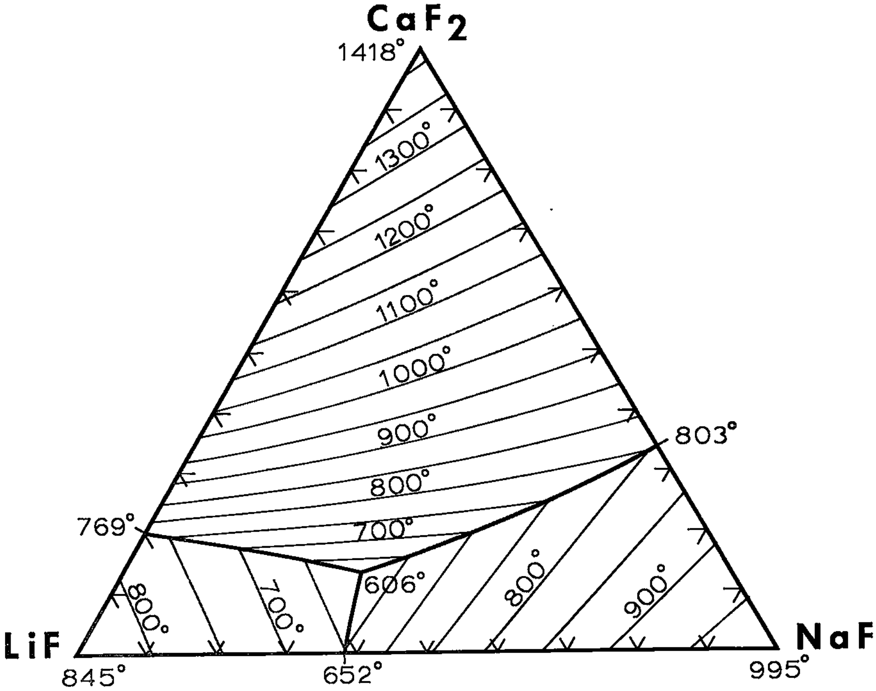

FIG. 1. Tracing of machine drawing of liquidus isotherms in the system LiF—NaF—CaF_2 (molar), computed and plotted by programme LQ3CBS-M5, with CON = 0.0.

sented, but the right—left variable is for the anion fraction and the up—down variable is for the cation fraction. The isotherms on the four liquidus surfaces are at temperature intervals that are set by the input data. The size of the square is fixed, and 0.1 ion fraction intervals are marked on the axes.

More detailed descriptions of the above computer programmes, with sample input and output data, are available for distribution. Punched card copies of the FORTRAN decks or column-binary compiled decks also are available.

The programmes for computing salt liquidus data tables, as described previously (Smith, 1965), have been translated into the FORTRAN IV language and copies of descriptions and card decks are available.

THE SYSTEM LiF—NaF—CaF_2

This system was chosen to test program LQ3CBS-M5 because (1) there are enough data on the liquidus curves in each of the three boundary binary systems to compute the required six sets of parameters, (2) each

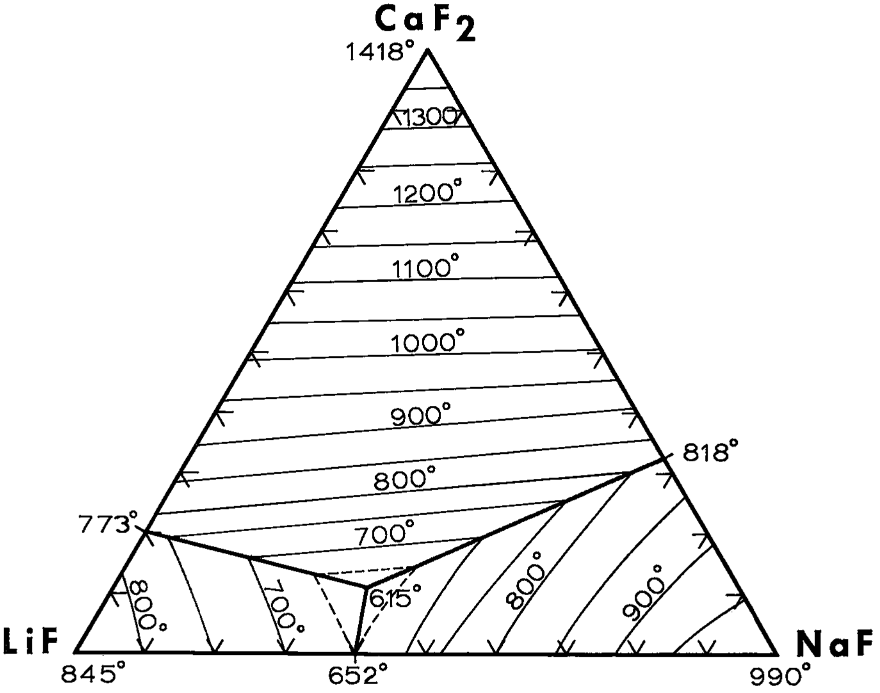

FIG. 2. Tracing of liquidus isotherms in the system LiF—NaF—CaF_2 (molar) as reported by Barton *et al.* (1959), with added 650° isotherm interpolated from the cotectic data.

of the binary systems has liquidus curves intersecting in simple eutectics with no indication of complexes stable with the liquid phase, (3) the components do not have the same valency, and (4) two independent measurements of the three liquidus surfaces in the ternary system are in substantial agreement.

Published data on liquidus curves in the binary systems were collected and used with programme LIQPAR-M3 to compute sets of liquidus parameters. (Sources of data and statistical processing are being organized for a later communication.) These parameters were used with programme LQ3CBS-M5 to compute and plot isotherms on the three liquidus surfaces. A tracing of the stable parts of the isotherms at intervals of 50° is shown in Fig. 1. In this plotting the valencies of Ca, Li, Na are as 2, 1, 1, and the vertices are labelled CaF_2, LiF, NaF. The value of the arbitrary exponent of the weighting factor was zero (*i.e.* CON = 0.0). A tracing of the liquidus isotherms reported by Barton *et al.* (1959) for this system is shown in Fig. 2. A re-run of the plotting programme with the same valencies for Ca, Li, and Na and the same value of CON gave results shown in Fig. 3. In this case the vertices are labelled CaF_2, Li_2F_2, Na_2F_2. A tracing of the liquidus isotherms reported by Bukhalova *et al.* (1959) for this system is shown in Fig. 4. The computed and measured eutectic points are summarized in Table 1.

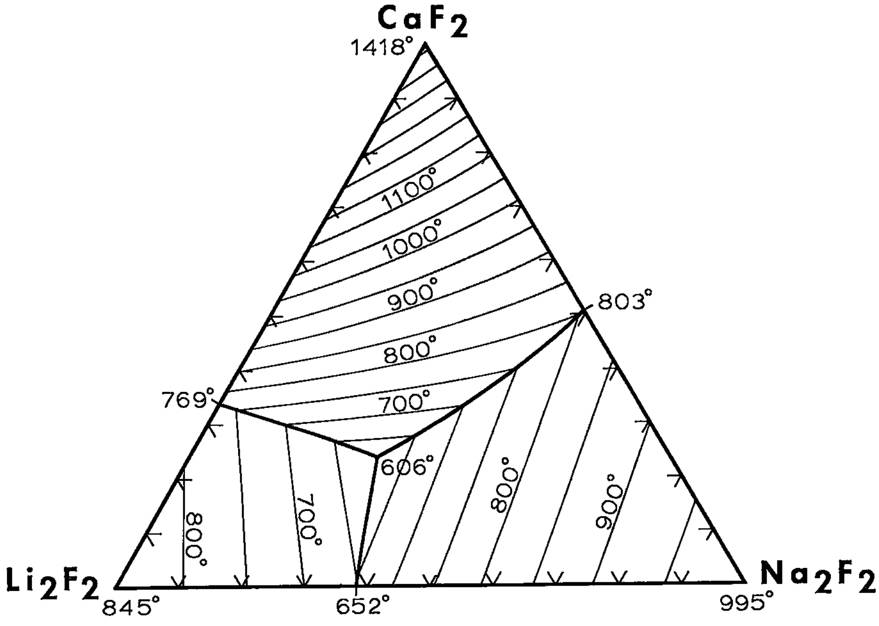

FIG. 3. Tracing of machine drawing of liquidus isotherms in the system Li_2F_2—Na_2F_2—CaF_2 (molar), computed and plotted by programme LQ3CBS-M5 with CON = 0.0.

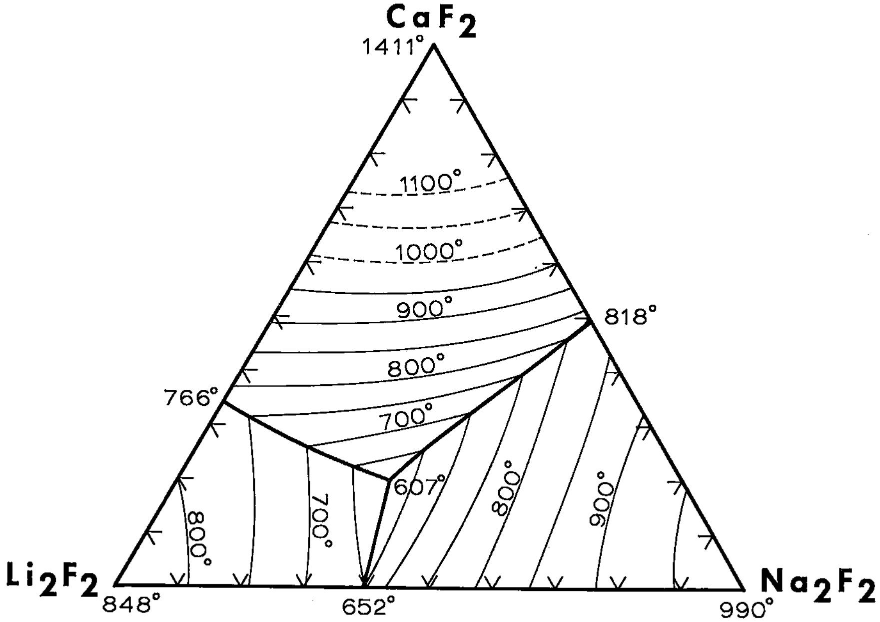

FIG. 4. Tracing of liquidus isotherms in the system Li_2F_2—Na_2F_2—CaF_2 (molar) as reported by Bukhalova *et al.* (1959).

TABLE 1. TENARY EUTECTIC POINTS

Solid Phases	Liquid Comp.	Temp. °C	Source of Data
LiF NaF CaF_2	0.53 0.36 0.11	615	Barton *et al.* (1959)
LiF NaF CaF_2	0.528 0.337 0.135	606	computed
Li_2F_2 Na_2F_2 CaF_2	0.465 0.335 0.200	607	Bukhalova *et al.* (1959)
Li_2F_2 Na_2F_2 CaF_2	0.465 0.297 0.238	606	computed
Li_2F_2 Li_2Cl_2 CaF_2	0.205 0.570 0.225	472	Bukhalova *et al.* (1949) (from the text)
Li_2F_2 Li_2Cl_2 CaF_2	0.128 0.647 0.225	472	Bukhalova *et al.* (1949) (from the phase diagram)
Li_2F_2 Li_2Cl_2 CaF_2	0.205 0.579 0.216	463	computed

THE RECIPROCAL SYSTEM CaF_2—LiF—$CaCl_2$—LiCl

This system was chosen to test programme LQDTRS-M5 because (1) binary liquidus relationships are well established, (2) the difference in free energy of the reciprocal salt pairs is small, and (3) liquidus surfaces in the ternary systems show little tendency toward liquid immiscibility. A complex salt in the CaF_2—$CaCl_2$ system (CaFCl) has a liquidus that extends into the ternary region but it was ignored in the computations.

Proceeding as above, the required binary parameters were computed (four being the same as before). A series of plots were made, varying the arbitrary factor (ARBFAC) that deforms the liquidus surfaces according to the value of the product of concentrations of the four simple ions. The calculated eutectic in the CaF_2—LiF—LiCl triangle was compared with that reported by Bukhalova *et al.* (1959) and it was found that a factor of 8.0 gave values of composition within limits of 1% of those reported in the text and 9° lower in temperature.

A tracing of the machine generated plot is shown in Fig. 5 (for CaF_2, Li_2F_2, $CaCl_2$, Li_2Cl_2 at the corners, conforming to the Russian practice).

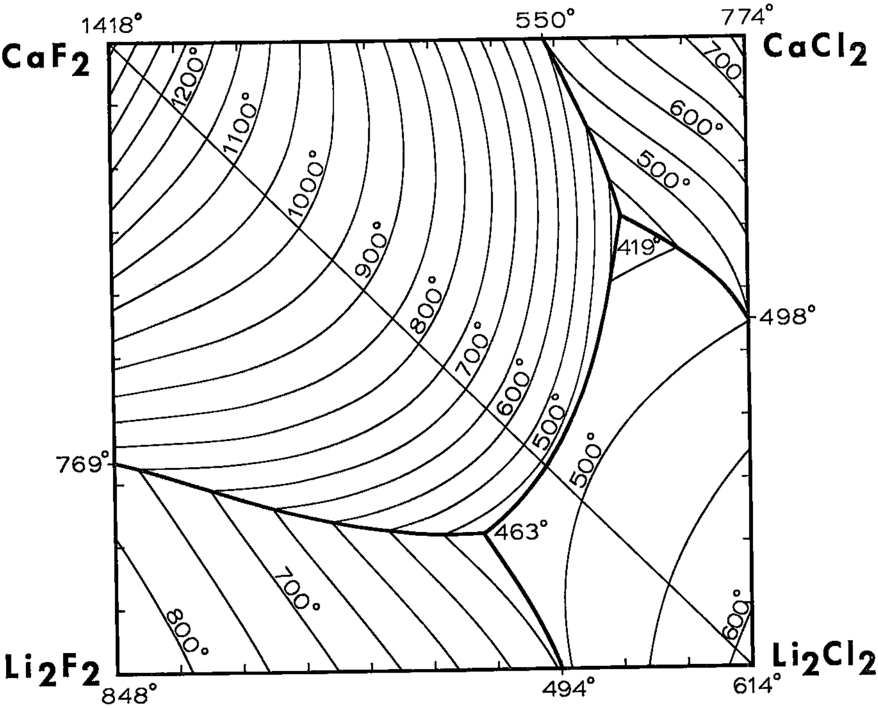

FIG. 5. Tracing of machine drawing of liquidus isotherms in the reciprocal system CaF_2—Li_2F_2—$CaCl_2$—Li_2Cl_2 (molar), as computed and plotted by programme LQDTRS-M2, with ARBFAC = 8.0.

A tracing of the isotherms reported by Bukhalova *et al.* (1959) is shown in Fig. 6 for comparison. Except for the neglect of the liquidus of the complex salt, Figs. 5 and 6 are fairly similar in most respects. We note, however, that the eutectic in the CaF_2—Li_2F_2—Li_2Cl_2 triangle of Fig. 6 is not at the composition stated in the text. This discrepancy is noted in Table 1. All of the other points are plotted correctly.

CONCLUSIONS

The plotting programs described above are useful for graphical display of binary liquidus curves and for rough approximation of ternary liquidus surfaces in simple and reciprocal salt systems. The method employed for approximating the effect of a difference in free energy of reciprocal salt pairs seems to be effective provided that the difference in energy is small.

ACKNOWLEDGMENTS

Grants from the National Research Council and the Geological Survey of Canada in aid of research on computation of phase relationships are

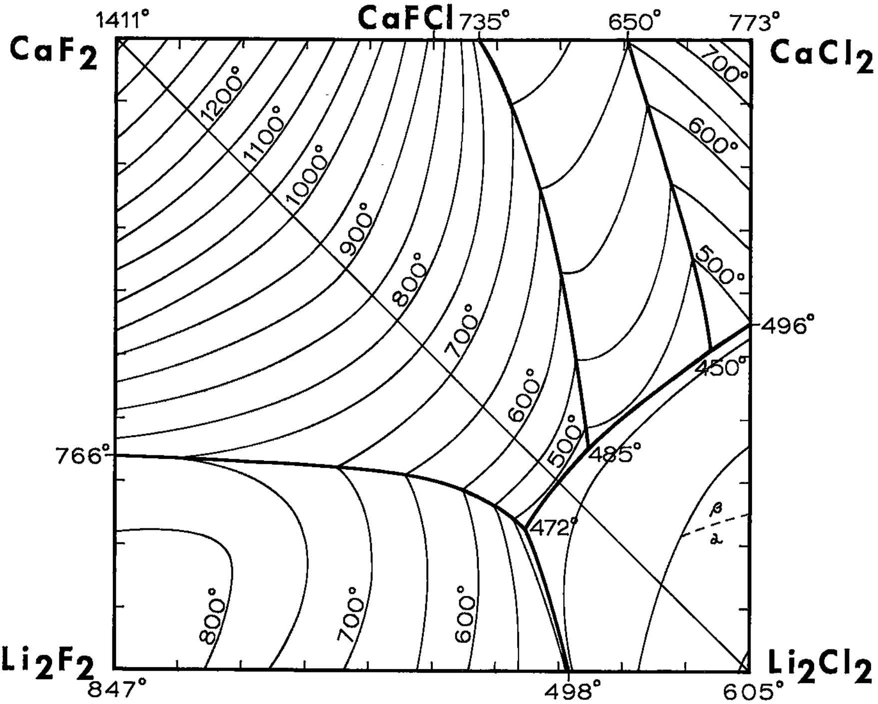

FIG. 6. Tracing of liquidus isotherms in the reciprocal system CaF_2—Li_2F_2—$CaCl_2$—Li_2Cl_2 (molar) as reported by Bukhalova & Bergman (1949).

gratefully acknowledged. Computing facilities were provided by the Institute of Computer Science of the University of Toronto.

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Manuscript received April 17, 1967