American Mineralogist, Volume 58, pages 1009–1015, 1973

Calculation of Binary Solvi With Special Reference to the Sanidine-High Albite Solvus

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Abstract

Application of the method of Scatchard (1940) to the direct calculation of binary solvi has the advantage of not requiring an iterative procedure based on an analytic expression of trial values. The method is used in the calculation of binary sanidine-high albite solvi based on data from Orville (1963) and Luth and Tuttle (1966). The data of the latter authors has been revised in that a systematic error was found in the original X-ray data. Differences arising in the calculated solvi are dependent on the determinative curve ($2\theta_{\bar{2}01}$ *vs* composition) employed in the reduction of the raw data, and on the stoichiometry of the starting materials. No adjustment of the calculated solvi based on the different determinative curves currently available will result in agreement of the three data sets of Luth and Tuttle (1966).

Thompson (1967) and Thompson and Waldbaum (1969a, b) have developed the Margules formulation of the Regular Solution Concept to a point where it is particularly useful in the analysis of experimental binary solvus data. In addition to providing a means for smoothing experimental data and predicting solvi under conditions where experimental data are lacking, the approach also provides a means for calculating thermodynamic excess functions and their dependence on pressure, temperature, and composition.

As outlined by Thompson and Waldbaum, the calculation of a smoothed solvus from a given set of experimental data on the composition of coexisting solvus pairs at a variety of pressure-temperature conditions involves:

1. Calculations of Margules mixing parameters of the G (Gibbs energy) function (W_{G1} and W_{G2}) for each pair of coexisting phases. The pertinent equations are 87a and 87b of Thompson (1967).
2. Obtaining regression equations for W_{G1} and W_{G2} as functions of temperature and pressure. The approach taken by Thompson and Waldbaum involves sum and difference quantities: $B_G = (W_{G1} + W_{G2})/2RT$; $C_G = (W_{G1} - W_{G2})/2RT$ as functions of reciprocal temperature and pressure.
3. Calculation of the solvus limb positions using the chemical potential equivalence conditions:

$$\mu_{1A} = \mu_{1B} \tag{1a}$$

$$\mu_{2A} = \mu_{2B} \tag{1b}$$

where A and B refer to phases, and 1 and 2 refer to components. The calculation outlined by Thompson and Waldbaum involves the use of the Newton-Raphson iteration with some set of trial, or initial, values for the composition of the coexisting phases.

Scatchard's Method

An alternative method presented by Scatchard (1940) has the advantage that a direct calculation of the binodal curve is possible, with no requirement of an analytic expansion for trial values. The chemical potential equivalence conditions are again the basis of this alternative method, as expressed in terms of the relative activities of the components in the coexisting phases:

$$RT \ln a_{1A} = RT \ln a_{1B} \tag{2a}$$

$$RT \ln a_{2A} = RT \ln a_{2B} \tag{2b}$$

The relative activity (a) of each component is calculated at specified increments of composition (N_2) at constant pressure and temperature using suitable equations. If the Margules formulation is employed, equations 80a and 80b of Thompson (1967, p. 353) are used. The computer algorithm[1] involves a search of $a_1 - a_2 - N_2$ space at constant temperature and pressure for the two compositions which satisfy equations (2a) and (2b). A graphical illustration of the method is given in Figure 1, similar to that given by Scatchard (1940). The determination of N_{2A} and N_{2B}, the equilibrium solvus pair, involves the location of point B in Figure 1. A solvus is constructed by repeating this process at increments of temperature for constant pressure (or at increments of pressure for constant temperature). If one is willing to plot the calculated activities as in Figure 1, then a simple desk calculator will serve for the calculation of the solvus. The precision of the method is limited by the precision of the raw data and by the increment of N_2 used in the search of $a_1 - a_2 - N_2$ space.

Application to the Alkali Feldspar Solvus

We have used the procedure to re-evaluate the data of Luth and Tuttle (1966) and Orville (1963) concerning the sanidine-high albite solvus. The Margules formulation was used exclusively and the direct W_{G1} and W_{G2} parameters were analyzed as functions of temperature. Only the 2 kbar data from both sources were considered. The analysis is similar in general format to that performed by Thompson and Waldbaum (1969b), but the conclusions differ somewhat.

A reanalysis of the Luth and Tuttle (1966) data is necessary in that the data as presented incorporate a systematic error. These authors observed that the compositions of cosynthetic feldspars crystallized at a given pressure and temperature appeared to depend on the molar $(Na_2O + K_2O)/Al_2O_3$ ratio of the starting materials. They presented data, largely for 2000 bars, on the compositions of the cosynthetic feldspars crystallized from peraluminous, $(Na_2O + K_2O)/Al_2O_3 < 1$, peralkaline, $(Na_2O + K_2O)/Al_2O_3 > 1$, and stoichiometric starting materials under hydrothermal conditions. Luth and Tuttle (1966, p. 1363) noted that the compositions of the phases were determined by the $2\theta_{\bar{2}01}$ method (Bowen and Tuttle, 1950) using a "working curve" based on a series of alkali feldspars prepared by Dr. H. Seck. The working curve was to be presented in a later paper. Luth and Querol-Suñé (1970) published chemical data and unit cell parameters for these feldspars. They noted that the starting materials were apparently peraluminous in that corundum (+quartz) was found in the crystallized products. This feature was also noted by Seck (1971, 1972). To relate $2\theta_{\bar{2}01}$ ($CuK\alpha_1$) and composition, Luth and Querol-Suñé (1970) give

$$N_2 = 20.467 - 0.9313\,(2\theta_{\bar{2}01}) \qquad (3)$$

for the alkali feldspar series they studied, but

$$N_2 = 19.885 - 0.9029\,(2\theta_{\bar{2}01}) \qquad (4)$$

for the high albite-sanidine series of Orville (1967). In terms of either equation, the compositions (in wt percent $KAlSi_3O_8$) listed by Luth and Tuttle (1966) are inconsistent with their associated 2θ values if $CuK\alpha$ to $CuK\alpha_1$ conversions are taken into account. Thus we must conclude that the "working curve" employed by Luth and Tuttle (1966) was inappropriate, and that a revision of their composition data is necessary.

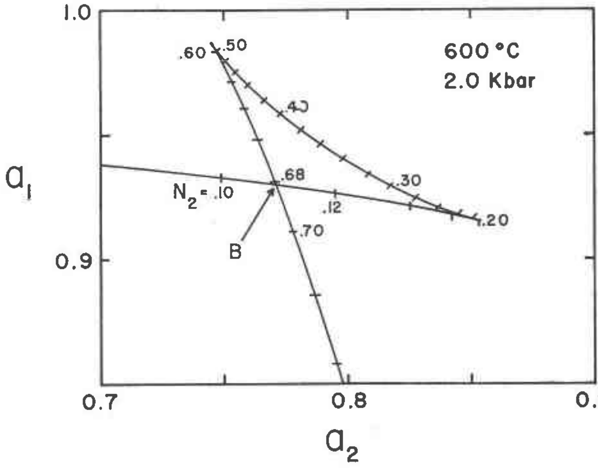

FIG. 1. Relative activities of $NaAlSi_3O_8$ (a_1) and $KAlSi_3O_8$ (a_2) at 600°C and 2 kbar. The compositions of the coexisting binodal phases are indicated as point B. The curve was calculated using the Margules parameters listed in Equation 1 in Table 1.

Margules Parameters

The raw data ($2\theta_{\bar{2}01}$) given by Luth and Tuttle (1966) permit evaluation of the effects of different starting materials and of determinative curves on the calculated Margules parameters and the solvi obtained from them. This analysis should provide some insight on

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[1] A program in the FOCAL language and a sample calculation have been deposited with the National Auxiliary Publications Service. To obtain a copy of this material, order NAPS Document 02203 from Microfiche Publications, 305 East 46th Street, New York, N. Y. 10017, enclosing $1.50 for microfiche or $5.00 for photocopies. Please check the most recent issue of this journal for the current address and prices.

the level of statistical significance to be attached to the Margules parameters in the calculation of thermodynamic excess and mixing functions. The Margules parameters obtained by linear least squares regression analysis, from the raw data of Luth and Tuttle (1966), are given in Table 1. The peralkaline data have been treated using only equation (3); the peraluminous and stoichiometric data have been treated using both equations (3) and (4). Also given in Table 1 are the Margules parameters we obtained using the four data points selected by Thompson and Waldbaum (1969a) from Orville's (1963) data. Separate columns in Table 1 give the calculated critical solution points for each data set. Critical solution points were obtained by calculation of the maximum spinodal temperature from equation (90) of Thompson (1967).

Calculated Binodal Curves

Figure 2a illustrates the differences in the calculated solvi when the raw data for all three (peralkaline, peraluminous, and stoichiometric) starting materials are analyzed using the same determinative equation, or working curve. It is not surprising that Figure 2a is very similar in form to that given by Luth and Tuttle (1966, Figure 6), though the coordinates differ somewhat. The Na- and K-limbs of the peralkaline and peraluminous solvi are clearly distinct. For the stoichiometric solvus its Na-limb essentially coincides with the Na-limb of the peraluminous solvus and its K-limb with the K-limb of the peralkaline solvus. Unit-cell refinements of X-ray powder diffraction data by Luth and Tuttle (1966) and by Luth and Querol-Suñé (1970) demonstrated that the unit-cell parameters for alkali feldspars crystallized from peralkaline starting materials differed significantly from those crystallized from peraluminous starting materials. It would thus seem inappropriate to use the same determinative curve for both the peralkaline and peraluminous raw data of Luth and Tuttle even though this was done by some authors, as well as to calculate the solvi shown in Figure 2a.

It seems reasonably clear that the determinative equation (4) based on the data of Luth and Querol-Suñé (1970) is appropriate for the peraluminous data. Since the unit-cell parameters of feldspars crystallized from both stoichiometric and peralkaline starting materials are similar to unit-cell parameters given by Orville (1967) for the sanidine-high albite series (Luth and Tuttle, 1966, Figure 7, Table 2) it seems reasonable to use determinative equation (3) for both the peralkaline and stoichiometric data. The effect of the different determinative equations on the calculated solvi is shown in Figure 2b for the stoichiometric starting materials. This effect is large and is in the same sense as that observed for the peraluminous starting materials.

Figure 3a illustrates the contrast in conclusions which can be drawn simply as a function of the determinative equation employed. The pattern shown in this figure is particularly satisfying if one is attempting to construct a model which stresses a smooth shift of the solvus limbs with changing ($Na_2O + K_2O$)/Al_2O_3 ratio. However, our conclusion is that the stoichiometric data should be analyzed in terms of equation (4), as in Figure 2a, *not* in terms of equation (3), as shown in Figure 3a.

The agreement between the solvi calculated from Orville's (1963) data, as selected by Thompson and Waldbaum (1969b), and the revised peralkaline

TABLE 1. Margules Mixing Parameters for Sanidine-High Albite Crystalline Solutions at 2 kbar

Data Set*	Eq.@	W_{H1} se# (cal)	W_{S1} se (cal/K)	ese# (cal)	W_{H2} se (cal)	W_{S2} se (cal/K)	ese (cal)	N	T_C (°C)	N_2(C) (m.f.)
1. Peralkaline	4	2332(2007)	-0.5291(2.2495)	269	11191(1627)	7.4453(1.8237)	218	11	670	0.38
2. Peraluminous	4	2069(1028)	-0.9159(1.1718)	104	7717(651)	3.9595(0.7418)	66	8	652	0.40
3. Peraluminous	3	-951(1534)	-3.8062(1.7490)	155	10985(817)	7.4721(0.9310)	83	8	649	0.37
4. Stoichiometric	4	2929(1134)	-0.3119(1.2671)	156	6902(647)	3.0510(0.7229)	89	12	665	0.42
5. Stoichiometric	3	1361(1492)	-1.6826(1.6669)	206	9298(731)	5.5375(0.8165)	101	12	664	0.39
6. Peralkaline-O	-	4181(525)	+1.8527(0.5972)	79	10662(900)	6.8447(1.0221)	134	4	670	0.35

* Data set 6 from Orville (1963), as selected by Thompson and Waldbaum (1969b). All other data from Luth and Tuttle (1966).

@ Equation 3 or 4 given in text.

\# se and ese refer to standard error terms for the coefficients (W_{H1}, W_{S1}, W_{H2}, W_{S2}) and the dependent variables (W_{G1}, W_{G2}) respectively.

N indicates the number of observations used in the least squares analysis.

T_C and N_2(C) are the calculated critical temperature and composition obtained from the given data set.

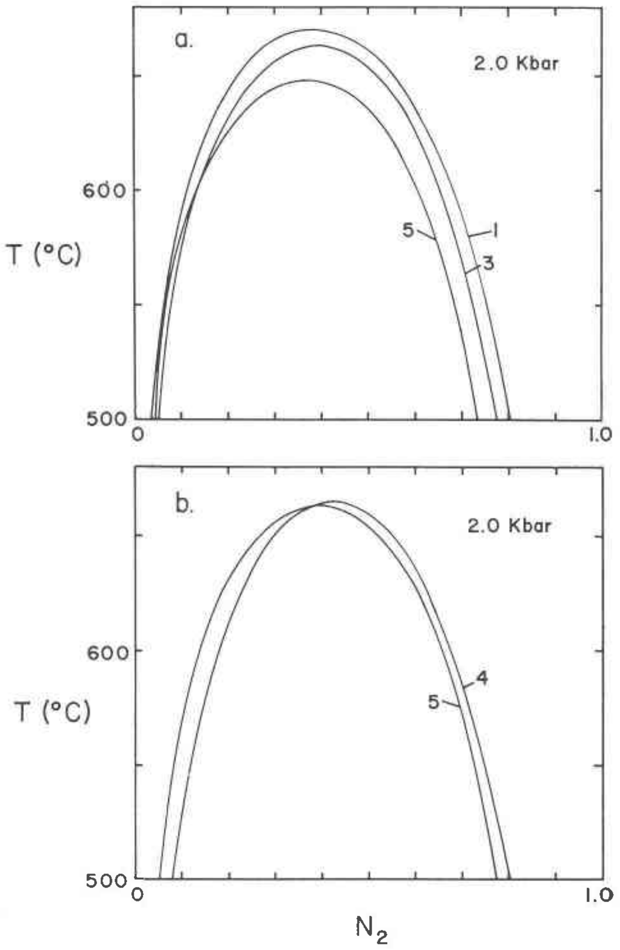

FIG. 2. Calculated alkali feldspar solvi at 2 kbar. Numbers on the curves refer to the equations listed in Table 1 from which the solvus was calculated.

data of Luth and Tuttle (1966) shown in Figure 3b appears to be satisfactory. The level of agreement is surprising in terms of the differences in the Margules parameters shown in Table 1. The solvus calculated directly from the "adjusted" Margules parameters given by Thompson and Waldbaum (1969b) is also shown in Figure 3b. It should be noted that the Margules parameters given by Thompson and Waldbaum (1969a) were adjusted to incorporate the effects of the equilibrium monoclinic-triclinic transformation in the sodic feldspars, but were based (in part) on the Luth and Tuttle (1966) peralkaline data.

On the basis of their graphic portrayal of the experimental results, Luth and Tuttle (1966) concluded that the three solvi representing crystallization from peraluminous, peralkaline, and stoichiometric starting materials were different. Thompson and Waldbaum (1969b) supported this conclusion with respect to the peralkaline and peraluminous data. However, in terms of their analysis, the stoichiometric and peraluminous data were not clearly separable. Thompson and Waldbaum (1969b) also concluded that the Luth and Tuttle (1966) peralkaline data were very similar to the peralkaline data of Orville (1963). Examination of solvi shown in Figures 2a, 3a, and 3b provides some support for these conclusions; however, examination of the Margules parameters and their standard errors suggests that these conclusions are on somewhat shaky ground.

Statistical Analysis

A simple statistical test to help evaluate differences between the Margules parameters, $W_{H(i)}$ and $W_{S(i)}$, which are regression coefficients, involves (1) calculation of the difference between the calculated value of $W_{G(i)}$ for any two regression equations as a function of temperature, and (2) comparison of this result with the calculated variance of this difference. The ratio of the difference and the square root of the variance serves to estimate t, which in turn serves to evaluate the significance level of the difference between two regression equations. Table 2 lists the temperature intervals over which the difference between the $W_{G(i)}$ values is significant at the 0.95 (two-sided Student's t test) level using this method. Only the region $500 \leq T(°C) \leq 700$ was evaluated in this connection in view of the data distribution. We infer that beyond the interval given in Table 2 the two regression equations do not yield $W_{G(i)}$ values which are significantly different.

As noted previously the preferred representation of the peralkaline, peraluminous, and stoichiometric raw data of Luth and Tuttle (1966) are equations (1), (3), and (4) of Table 1. Considering only the analysis for these regression curves, as given in Table 2, the three regression equations for both W_{G1} and W_{G2} appear to be significantly different at the 0.95 probability level over a relatively large temperature interval. The effect of the determinative curve used is illustrated by comparing cases 2 and 3 or 4 and 5 (Table 1) as shown in Table 2. In the case of different treatments of the peraluminous data (2 and 3) and of the stoichiometric data (4 and 5), the regression curves are also distinct over a significant temperature interval. In fact the temperature interval may be considerably greater in this case.

Conclusions

Although the analysis of the Luth and Tuttle (1966) data is complicated by lack of certainty as to which determinative curve (if either) is appropriate, it appears that no currently available set of determinative curves can bring all three data sets into agreement. Regardless of the cause underlying the differences in the solvi, the differences appear to be real and significant. More recent studies by Seck (1972) and by Luth, Martin, and Fenn (1973) confirm differences between solvi obtained from peraluminous and those from peralkaline starting materials. At low ($P \leq 2.5$ kbar) pressures, the differences between the peralkaline and the peraluminous solvi are similar to those shown in Figure 3a.

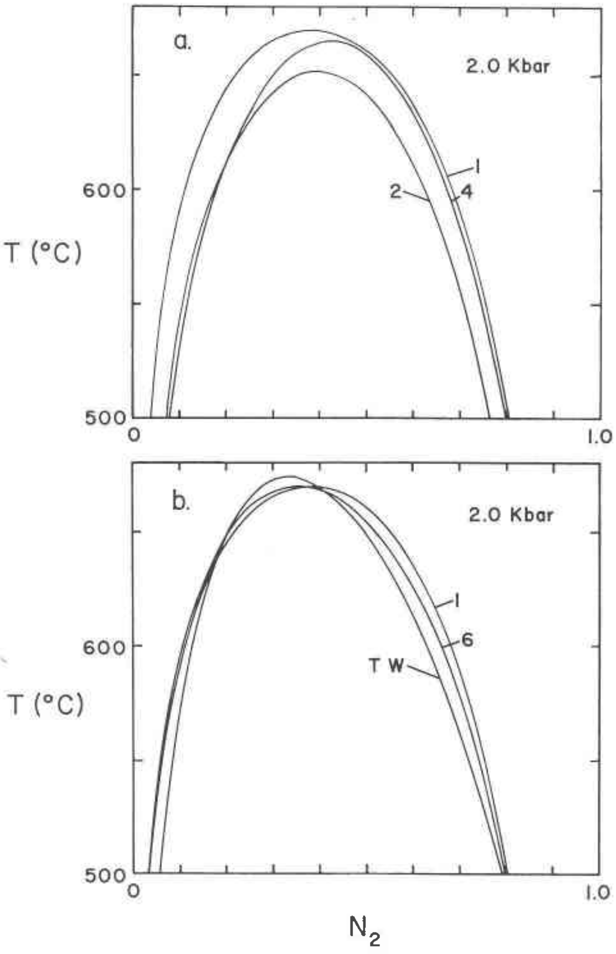

FIG. 3. Calculated alkali feldspar solvi at 2 kbar. As in Figure 2 the numbers refer to the equations of Table 1. Refer to the text for a discussion of the significance of each solvus in this Figure and in Figure 2.

TABLE 2. Temperature Intervals Over Which the 2 kbar Margules Are Significantly Different

Data Set	1	2	3	4	5	6
1	-------	605-630	500-655	545-690	610-630	585-700
2	500-660	-------	500-670	505-685	NONE	545-700
3	565-665	500-635	-------	500-700	500-670	500-620
4	500-660	NONE	500-635	-------	510-680	500-700
5	565-645	545-650	615-625	500-645	-------	575-700
6	NONE	500-670	545-690	500-670	500-650	-------

The temperature intervals given above, in °C, are those over which the Margules parameters W_{G1} (upper triangular matrix) and W_{G2} (lower triangular matrix) are significantly different at the 0.95 level using the Student's t test in comparing the two data sets, from Table 1, shown in the first column and row.

Appendix: Procedure for Computation of Binary Solvus Compositions

The following procedure is an outline of the steps involved in calculation of binary solvi. The method involved is that used graphically by Scatchard (1940). Analytic expressions are derived from the presentation by Thompson (1967) for the most part. A FOCAL program which has been used on an 8K PDP 8/e has been deposited with NAPS.[1] Duplicate punched paper tape copies of the program are available from the authors.

Procedure

1. Obtain functional relationships for W_{G1} and W_{G2} (Thompson, 1967) such as:

$$W_{G1} = A_1 + B_1 T(°\mathrm{K}) + C_1 P(\mathrm{bars}) + D_1 PT; \quad (1a)$$

$$W_{G2} = A_2 + B_2 T + C_2 P + D_2 PT \quad (1b)$$

by standard least squares techniques from the experimental data.

2. Calculate the critical constants from the maxima on the spinodal curve using:

$$0 = \frac{\alpha RT}{N_1 N_2} + 2W_{G1}(1 - 3N_2) + 2W_{G2}(1 - 3N_1) \quad (2)$$

which can be transformed to:

$$T_s = \alpha R(6N_2^3(W_{G2} - W_{G1}) + 2N_2^2(4W_{G1} - 5W_{G2}) + 2N_2(2W_{G2} - W_{G1})) \quad (3)$$

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[1] Footnote on page 1010.

where T_s is the spinodal temperature for a given N_2, and $N_1 = 1 - N_2$, with other symbols as defined by Thompson (1967). Equation (2) is from Thompson (1967, p. 356, equation 90).

3. Calculate binodal (solvus) compositions which simultaneously satisfy the conditions:

$$a_{1A} = a_{1B}, \tag{4a}$$

$$\text{and} \quad a_{2A} = a_{2B} \tag{4b}$$

a_{ij} is the relative activity. A and B refer to phases, 1 and 2 refer to components as in Thompson (1967) $a_{ij} = N_{ij}\gamma_{ij}$. $a_{1A} = N_{1A}\gamma_{1A} = (1 - N_{2A})\gamma_{1A} = \gamma_{1A} - N_{2A}\gamma_{1A}$ and from Thompson's (1967, p. 352) equations 80a and 80b:

$$\gamma_{1i} = \exp\left((N_{2i}^2/RT)(2W_{G2} - W_{G1} + 2N_{2i}(W_{G2} - W_{G1}))\right) \tag{5}$$

$$\gamma_{2i} = \exp\left((1/RT)(W_{G2} + 2N_{2i}(W_{G1} - 2W_{G2}) + N_{2i}^2(5W_{G2} - 4W_{G1}) + 2N_{2i}^3(W_{G1} - W_{G2}))\right) \tag{6}$$

For convenience let: $X = 2W_{G2} - W_{G1}$, (7a)

$$Y = W_{G1} - W_{G2}; \tag{7b}$$

$$\text{then} \quad X - 3Y = 5W_{G2} - 4W_{G1}. \tag{7c}$$

Then

$$a_{1A} = (1 - N_{2A}) \exp\left((N_{2A}^2 X - 2N_{2A}^3 Y)/\alpha RT\right) \tag{8}$$

$$a_{1B} = (1 - N_{2B}) \exp\left((N_{2B}^2 X - 2N_{2B}^3 Y)/\alpha RT\right) \tag{9}$$

$$a_{2A} = N_{2A} \exp\left((X + Y - 2N_{2A}X + N_{2A}^2(X - 3Y) + 2N_{2A}^3 Y)/\alpha RT\right) \tag{10}$$

$$a_{2B} = N_{2B} \exp\left((X + Y - 2N_{2B}X + N_{2B}^2(X - 3Y) + 2N_{2B}^3 Y)/\alpha RT\right) \tag{11}$$

The procedure which we have used in calculation of the isobaric solvus involves a search of $N_{2A} - N_{2B}$ space at a specific pressure and temperature to find the unique N_{2A} and N_{2B} values which satisfy the simultaneous equilibrium conditions given in equations 4a and 4b. The nature of the search is readily visualized in terms of Figure 1, a plot of calculated a_1 and a_2 values at 600°C and 2 kbar for a data set pertinent to the alkali feldspar system ($1 = NaAlSi_3O_8$, $2 = KAlSi_3O_8$). This diagram is identical in form to that given by Scatchard (1940). Using this diagram for the explanation we consider the following stages in the calculation.

1. a_{1A} is calculated for $N_{2A} = 0.08$, then a_{1B} is calculated for $N_{2B} = 0.74$. Since $a_{1B} < a_{1A}$ the trial N_{2A} and N_{2B} values are beyond the solvus limbs.
2. Then N_{2B} is reset to 0.72, and a_{1B} is recalculated. Again, $a_{1B} < a_{1A}$, so the process is repeated for $N_{2B} = 0.70$, 0.68, and 0.66 in sequence. When $N_{2B} = 0.66$ we find that $a_{1B} > a_{1A}$. N_{2B} is reset to 0.68, and the decrement in N_{2B} is changed from 0.02 to 0.005, and the process repeated, using smaller and smaller decrements of N_{2B} until the desired value ($N_{2B} = .676$) is obtained. Note that N_{2A} has been held constant at 0.08 throughout this process, and we have been concerned with the evaluation of a_{1A} and a_{1B}.
3. a_{2A} and a_{2B} are calculated for $N_{2A} = 0.08$ and $N_{2B} = 0.676$. Since $a_{2A} < a_{2B}$, N_{2A} is clearly outside the solvus limb and N_{2B} must lie inside the other solvus limb. Consequently N_{2A} is reset to 0.10 and N_{2B} to $0.676 + 0.05 = 0.726$ and the process outlined in (1) and (2) is repeated. Increments of N_{2A} and N_{2B} are reduced such that the desired N_{2A} and N_{2B} values of 0.110 and 0.682 are obtained, for this pressure and temperature.
4. A new temperature (and pressure if desired) is reset and the entire process is repeated in order to obtain new values.

This method is extremely flexible in terms of the increments in N_{2A} and N_{2B} used in the evaluation process, and the specific initial N_{2A} and N_{2B} trial values (0.08 and 0.74 in the above example) employed.

Acknowledgments

This research has been supported by the National Science Foundation (NSF GA 1684). Professor D. R. Waldbaum's critical analysis of this paper led to considerable improvement and is very much appreciated.

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Manuscript received, November 17, 1972; accepted for publication, July 10, 1973.