Segregation in ternary solutions

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(Received July 12, 1976)

The spinodal surface and the stable binodal surface must touch tangentially at any extremum/saddle point and along any consolute line. Because of this, the most convenient way to study immiscibility in a ternary is to calculate the spinodal surface. Other authors have accomplished this in a binary regular and subregular solution and in a ternary regular solution but the derived equations are not applicable to a ternary subregular solution or to a Kohler solution. The equation for the spinodal in a ternary Kohler solution is herein derived so that now it is possible to study immiscibility using the spinodal in any ternary Kohler solution, including a subregular ternary solution.

MEIJIRING used the spinodal equation to derive relations which characterise the form of segregation in a ternary regular solution. When the “effective” regular solution parameter is substituted into these relations, they can be used as a rough approximation to characterise segregation in a subregular ternary solution; the number of peaks and saddles in the ternary solvus can be predicted but the temperature/composition of them cannot. This rough scheme is used with a graph which shows that the composition of the critical point on a subregular binary solvus is only a function of the ratio of the two subregular parameters.

The temperature dependence of subregular solution parameters is capable of exerting a strong control on the unique features of a ternary spinodal, so that a more exact study of immiscibility must involve the calculation of the spinodal surface using temperature dependent solution parameters. A model spinodal for the ternary feldspar system at 1 kb is calculated using temperature dependent subregular solution parameters.

INTRODUCTION

MEIJIRING (1950, 1951) has skillfully studied the characterization of regular ternary solutions which show segregation. Using the equation for the ternary spinodal he derived a series of relations which specify the composition and temperature of any ternary extremum. His treatment of the binodal results in relations for trace element distribution and also for special tie-line configurations. Some very complicated terminations of ternary solvi can be discerned mathematically according to the relations of MEIJIRING (1950, 1951).

The simplicity of MEIJIRING’s equations is lost when it is assumed that the binaries are sub-regular solutions. For example, assuming the model of KOHLER (1960) is applicable to a subregular ternary (see BARRON, 1976), a relation for the spinodal (A7) can be derived but it consists of the product of two seven-term expressions minus the product of two eight-term expressions while MEIJIRING’s spinodal equation for a regular ternary consists of a sum of ten simple terms (18). Because of this large size of the analogous expressions it was decided not to consider an exact explicit scheme analogous to MEIJIRING’s approach but instead to show how MEIJIRING’s relations can be used as an approximation to predict the existence of extremum and saddle structures in ternary solvi where the binaries are sub-regular solutions. The phase complexities that can be demonstrated by MEIJIRING (1950, 1951) cannot be considered in such an approximate treatment and they would have to be delineated by computer calculation of the ternary binodal.

MEIJIRING (1950) showed how convenient the spinodal surface is in characterizing the shape of solvi in ternary regular solutions. The fact that this convenience will also be true for a more complicated solution model indicates the necessity of deriving an expression for the
spinodal in a general ternary solution.

Discussion

Characterization of a regular ternary and the migration of the consolute line

One of the most significant features of a ternary solvus is whether or not it has a maximum inside the ternary. This situation is precisely handled by MEIJIRING’s equations (1950, equations 9 and 29) as follows: for regular solution model parameters a > b > c, c < 0, when b – c > a this implies a ternary maximum (condition 1) and when a > b – c this implies a steady drop in temperature from the “a” solvus to the next largest solvus, if any (condition 2). When condition 1 is met the following two equations (after MEIJIRING, 1950) define the position of the ternary solvus apex.

\[ N_1 = 0.5 \]
\[ N_2 = (c + b - a)/4c \]
\[ RT = -L/8c \]

where \[ L = a^2 + b^2 + c^2 - 2ab - 2bc - 2ac \]

Note that the consolute line, which must pass through the ternary solvus apex, migrates along the line \( N_1 = 0.5 \) at least as far as the apex.

This migration is radically different from the situation when c < 0, a > b – c because then the consolute line migrates from \( (N_1 = 0.5, N_2 = 0.5) \), to \( (N_2 = 0.5, N_3 = 0.5) \), i.e., \( N_2 \approx 0.5 \), according to MEIJIRING. In general it appears that the consolute line will migrate from the highest binary solvus in a general direction towards the next highest binary if the highest binary solvus drops in temperature on entering the ternary. As an example of MEIJIRING’s predictions, GANGULY (1976) has calculated regular solution values for the binaries on Grossular-Andradite-Uvarovite (G,A,U) and finds that condition 1 holds so that there should be a ternary apex in the solvus which he calculates is at the position \( N_1 = N_A = 0.5, N_2 = N_U = 0.404, T = 1,002^\circ C \). GANGULY (1976) calculated the spinodal using MEIJIRING’s equation (18) and estimated the position of the 800°C isotherm on the binodal. The activity matching algorithm described in BARRON (1976) has been used to calculate the complete solvus down to 400°C and Fig. 1 shows the results. The dotted lines represent icophases which are, in this case, isocons of Grossular in the coexisting phase and along with the isotherms they completely determine the solvus. This can be demonstrated by considering a garnet of composition \( N(A,G,U) = (0.2, 0.3, 0.5) \) which plots at 795°C and

Fig. 1. Binodal surface in Andradite - Grossular-Uvarovite calculated for the regular solution model parameters of GANGULY (1976).
Segregation in ternary solution indicates the coexisting garnet has $N_G = 0.12$. These two items of data are sufficient to position the coexisting phase on the opposite side of the consolute line at $T = 795^\circ C$, $N_G = 0.12$. There is a certain amount of error associated with the computer calculation of the binodal: In order to limit the computing costs the activity matching error limits have been taken as $\sigma$ (activity) $\leq 0.002$. While this is acceptable away from the consolute line and ternary apex, this activity error allows an error of $0.01 - 0.02$ mole fraction near the consolute line and especially near the ternary apex. It was of great assistance, in interpreting the position of the consolute line within those limits of error, to know the theoretical position of the apex. Furthermore the compositional curvature of the consolute line between the ternary apex and the binary Andradite-Uvarovite is probably caused by this error in activity matching.

Characterization of the binary solvus in a subregular solution. The migration of the consolute line across the ternary is the locus which will be used to approximate conditions 1 and 2 for a subregular ternary. This migration path will be approximated by conditions mentioned above (see after equation 4) so it is necessary to know the positions of the maximum in the subregular binaries. MEIJERING (1950) showed that the spinodal is the easiest equation to treat for critical composition so we start from the equation of a binary subregular spinodal curve which is given in THOMPSON (1967, equation 90)

where $Y = \frac{RT}{2} (\text{spinodal})$

$$= -N_1 N_2 \left[ W_{12} \left( 1 - 3N_2 \right) + W_{21} \left( 1 - 3N_1 \right) \right]$$

$$= (2N_1 - 5N_2 + 3N_3)W_{12}$$

$$+ (4N_2 - 3N_3 - N_1)W_{21} \quad (5a)$$

The solvus has its maximum where the spinodal has its maximum value which is when $dY/dN_i = 0$ or

$$(2 - 10N_1 + 9N_2^2)W_{12}$$

$$+ (8N_1 - 9N_2^2 - 1)W_{21} = 0 \quad (6)$$

Putting $Q = W_{12}/W_{21}$ and collecting terms we arrive at

$$9N_2^2 (Q - 1) + N_1 (8 - 10Q) + 2Q - 1 = 0 \quad (7)$$

that

$$N_1 = \frac{-8 + 10Q \pm \sqrt{(8 - 10Q)^2 - 36(Q - 1)}}{18/(Q - 1)}.$$  

$$(2Q - 1) \quad (8)$$

The portion under the square root reduces to $28 + 28Q^2 - 52Q$ and since $N_1 < 0.5$ for $Q > 1$ then $N_1 = \frac{[10Q - 8 - \sqrt{28 + 28Q^2 - 52Q}]}{18/(Q - 1)}$ for $Q > 1, W_{ij} > 0$.

$$(9)$$

This equation demonstrates that the solvus maximum occurs at a composition that is determined only by the ratio of $W_{12}/W_{21}$ and not by their real values. Note that when $W_{ij} = 0$ this is still

Fig. 2. Standard curves for the determination of the composition and temperature of the critical point on a binary subregular binodal/spinodal.
true because the quadratic solution of the reduced form of (6) is then independent of $W_{ji}$ with solutions

$$N_1 = \frac{0.26}{1+Q} \text{ for } W_{21} = 0 \text{ and } N_1 = \frac{0.74}{1+Q} \text{ for } W_{12} = 0.$$ 

The locus of (9) is quite a useful item and has been calculated on Fig. 2, curve: $(Q > 1)$. The compositional position of the maximum of a subregular solution model binary is immediately known if $Q > 1$ is known, or vice versa. For the situation where $W_{12} W_{21} < 0$ and $W_{12} > 0$, $N_1 < 0.5$ and $Q < 0$ so that the correct root from (8) is

$$N_1 = \frac{10Q - 8 + \sqrt{28 + 28Q^2 - 52Q}}{18/(Q-1)}. \quad (10)$$

This function is also shown on Fig. 2 and allows the compositional positioning of the solvus maximum when the $W$ parameters have the opposite sign but $W_{12} > 0$. As expected, the more negative $W_{21}$, the further the maximum is displaced away from $N_1 = 1.0$.

In terms of the critical temperature we may also produce a parametric curve, similar to Fig. 2, which displays a function of the critical temperature versus a function of the subregular model parameters. Equation (5a) at the critical point $(T_c, N_1)$ can be modified to

$$RT_c/W_{21} = 2N_1 (4 - 5Q) + 2 (2Q-1)/3 \quad (5b)$$

using the definition of $Q$ and (7). Now $N_1$ mentioned in this equation (5b) is the critical composition and is only a function of $Q$, so that the parameter $RT_c/W_{21}$ is also only a function of $Q$. A graph of this function has been produced by substituting appropriate pairs of $Q, N_1$ into (5b) and the result is also shown on Fig. 2. The two curves are nearly straight lines.

Characterization of the ternary solvus in a subregular solution  The model of KOHLER (1960) is a general excess free energy model which describes how to mix the binary excess free energies with a dilution factor to obtain a multicomponent excess free energy. The forms of the binary excess free energies are completely unspecified and can be according to any solution model, even though KOHLER’s model is derived by analogy with the regular solution model. BARRON (1976) examined a ternary subregular solution using KOHLER’s model versus WOHL’s model (WOHL, 1946, 1953) and showed that both models gave somewhat comparable results with regard to the solvus isotherm, the partitioning curves and the slope of tie-lines when compared to the experimental work of SECK (1971) on Anorthite-Orthoclase-Albite at 900°C, 0.5 kb. KOHLER’s model has a simplicity that is easily adapted to rough graphical treatment. For instance, KOHLER’s model for $G^x$ in a ternary is simply

$$G^x = (N_1 + N_2)^2 G^x_{12} + (N_1 + N_3)^2 G^x_{13} + (N_2 + N_3)^2 G^x_{23} \quad (11)$$

where $G^x_{12}$ is the value of $G^x_{12}$ in the binary 12 at a normalized composition of $N_1/(N_1 + N_2)$. In a ternary this normalization is accomplished graphically by following a straight line from the opposite apex to the binary in question. When binary graphs of $G^x_{ij}$ or $G^x_{ij}/N_i/N_j$ are placed along the sides of the ternary plot, this graphical procedure very quickly allows estimation of the parameter $G^x_{ij}$ or the “effective” regular solution model parameter $W$ (binary $ij$ at $N_i/N_j = G^x_{ij}/N_i/N_j$)

$$W = \frac{N_i = N_i/(N_i + N_j)} \quad (12)$$

To create an approximate analogy with the relations of MEIJIRING (1950, 1951) we need to compare values of $a$, $b$ and $c$ and keeping in mind the simplicity of a rough graphical treatment of KOHLER’s model we will use values of the “effective” regular solution model parameter as estimates for $a$, $b$ and $c$. The following treatment pertains to a KOHLER model of a ternary subregular solution using the above graphical determination of the “effective” regular solution model parameter.

The first example will be to investigate the situation where a ternary has a central immiscibility field which is free standing from the binary solvi; the binary solvi enter the ternary with dropping temperatures at the same time as a ternary peak exists in the core of the ternary. If we assume the binary solvi peak at $N_1 = 0.5$, the conditions can be expressed as

$$W_{32} - W_{31} < (W_{12} + W_{21})/2 \text{ for } W_{32} > W_{31} \quad (13)$$

$$W_{32} + W_{23})/2 > W_{12} - W_{13} \text{ for } W_{12} > W_{13} \quad (14)$$
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and \((W_{32} + W_{23}) - (W_{32} + W_{13}) > (W_{12} + W_{21})\) in

(15)

the core of the ternary for

\[W_{12} + W_{21} > W_{23} + W_{23} > W_{13} + W_{31}.\]

(16)

The first two inequalities mean that the binary solvi in 12 and 23 will drop into the ternary with temperature decreasing (i.e. \(a > b - c\)) while the third one means that in the middle of the ternary, \(b - c > a\), and a ternary maximum should result. The implied "for" conditions are a reflection of MEIJIRING's (1950) definition of \(a > b > c\). In actual fact the sums \((W_{12} + W_{21})\) etc. in (13) and (14) should be replaced by the effective regular solution parameter (12) at the critical composition, while the sums \((W_{32} + W_{23})\) etc. in (15) and (16) should be replaced by the effective regular solution parameters at the ternary critical composition which is as yet unknown. For the form of (15) and (16) it has been assumed that the critical composition is \(N_1/N_2/N_3 = 1/3\). A set of \(W(I, J)\) which satisfies (13 to 16) is, for \(I = \) row number, \(J = \) column number, in cals/mole:

\[
\begin{array}{ccc}
0 & 1000 & -1900 \\
-1000 & 3000 & 0
\end{array}
\]

(17)

The critical binary compositions are obtained from Fig. 1 with \(Q = 8\) and \(Q = 3.5/3\). Now the consolute line should extend from \((N_2 = 0, N_1 = 0.73)\) to \((N_1 = 0, N_3 = 0.56)\) because the binary solvi will drop going into the ternary \((a > b - c)\). Graphical determination of where \(a + c - b = 0\) with \(a = W(12)\) at \(N_i\) on Fig. 3 indicates there should be a saddle at about \(N(1,2,3) = (0.36, 0.37, 0.27)\) while graphical determination of where \(a + c - b = 0\) with \(a = W(23)\) at \(N_i\) on Fig. 3 indicates there should be a saddle at about \((0.04, 0.43, 0.53)\). At the first point \(a = 4,600, b = 3,200, c = -1,400\) so that \(L = 2.576 \times 10^7\) while (3) indicates \(T = 884^\circ\). At the second point \(a = 3,300, b = 1,500\) and \(c = -1,800\) so that \(L = 2.5 \times 10^7\) and \(T = 555^\circ\). To summarize, the criteria analogous to MEIJIRING's relations predict that there will be two saddles separated by a ternary maximum. A comparison of the predicted temperatures of one of the saddles (555°C) with the nearest maximum in the binary 23 (555°C) indicates that the approximations will not always be able to indicate the temperature of the saddles, and as a result may not always indicate their approximate position. Furthermore there doesn't seem to be any way of estimating either the position or the temperature of the ternary maximum. At this point we obviously need to check the predictions made and see if their accuracy warrants further treatment along the above lines.

The most powerful tool which MEIJIRING used to derive his relations for characterizing ternary solvi was determined from a consideration of the equation of the ternary spinodal. The spinodal for a ternary regular solution, is simply expressed as, modified after MEIJIRING (1950, equation 8),

\[
(\frac{RT}{2G})^2 - 2G \frac{RT}{1N_1N_2N_3} = 0
\]

(18)

The significance of the spinodal equation is composed of several features:

i) Where the ternary spinodal surface has peaks, saddles or basins, these points will exactly correspond to analogous structures on the stable binodal. The two surfaces also correspond along consolute lines.

ii) A binodal is not easy to calculate and may involve several man hours and several hundred seconds of computing. Even after it is calculated there is no guarantee that all of it or any portion of it is stable. This can only be established by comparing the spinodal surface with the binodal surface.

iii) The spinodal is usually simple to calculate because it involves only one composition.
These points are just as applicable to a subregular ternary solution as to a ternary regular solution so the spinodal surface should be the key to use in studying segregation in subregular ternary solutions.

The steps which led Meijiring (1950) to the equation of the regular ternary spinodal can also be followed with regard to a ternary Kohler solution. This is accomplished in appendix A. The situation for subregular solutions may be considered by simply using the appropriate substitutions in the general equation (A13). Figure 4 shows the calculated spinodal surface for the trial \( W(I, J) = (17) \). The spinodal surface indicates that there is only one saddle (at 530°C) while there is a marked break in slope at 1,400°C which could be modified into a maximum and saddle by increasing the contrast in (15). The correspondence between these features and the predicted structures is not very good which indicates that the characterization scheme can only be used to suggest the existence of ternary extremum/saddle structures and is only a rough approximation.

A second example of is different from the proceeding one because the rough characterization predicts there will be a ternary maximum but only one saddle: Near \( N_3 = 0.68 \) in the binary 23, \( b-c > a \) so the solvus from the binary 23 will enter the ternary system with increasing temperature while the situation near \( N_1 = 0.5 \) in the binary 12 is \( b-c < a \) so that the solvus in the binary 12 will enter the ternary with decreasing temperature. The situation in the core of the ternary is \( b-c > a \) so there should be a ternary maximum but only one saddle. The graphical treatment used on the previous example did not yield results accurate enough to justify its use so we proceed straight to the calculated spinodal which is presented in Fig. 5. The characterization scheme has correctly predicted that only one saddle would occur.

Temperature dependent solution parameters

The relations of Meijiring (1950) are made more complicated if the regular solution parameters are temperature dependent. Clearly if the subregular solution parameters are strongly temperature dependent the approximate characterization will work best if approximately the right temperature is chosen to begin with. With regard to calculation of the spinodal surface it has been found that successive approximation of the spinodal temperature converges very rapidly to a consistent temperature. Figure 6
Fig. 5. Calculated spinodal for a ternary subregular KOHLER solution with $W_{I,J}$ as indicated in cal/mole.

shows an example of the spinodal of a model for the ternary feldspar system using solution model parameters calculated at 1,000°C, 1 kb. While the parameters in Ab-Or are after THOMPSON and WALDBAUM (1969), the others are from a range of data which will be discussed in BARRON (in prep). The next diagram, Fig. 7, is the spinodal calculated as a model for the ternary feldspar system using temperature dependent solution parameters. This dependence is according to the equation


where

$$D(I,J) = 8,072 \begin{bmatrix} 0 & 8,607 & 1,520 \\ 6,494.18 & 6,326.7 & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 0.1 \\ 0.1 \end{bmatrix} + P* F(I,J) + H(I,J) \begin{bmatrix} 0.1 \\ 0.1 \\ 0.0925 \end{bmatrix}$$

and

$$H(I,J) = 0 \begin{bmatrix} 0 \\ 0 \end{bmatrix} + P* F(I,J) + H(I,J) \begin{bmatrix} 0 \\ 0 \end{bmatrix} -3.8565 \begin{bmatrix} 0 \\ -3.8565 \end{bmatrix}$$

In this particular example the geometry of the spinodal is quite simple and is not strongly changed by introducing the temperature dependence. Figures 6 and 7 correspond along the 1,000°C isotherm and close to the binary An-Or, which has an unknown and assumed zero temperature dependence. However, in many other cases a change of 250° in the spinodal surface (i.e. the difference between the Ab-Or maximum in Figs. 6 and 7) will be sufficient to bury or reveal a ternary critical point, so that accurate use of the spinodal equation requires inclusion of the temperature dependence of the solution parameters.

**List of Symbols**

- $N_I$: mole fraction of component I
- $N(I,J,K)$: mole fractions of component I, J, and K
- $a,b,c$: regular solution model parameters
- $W_{I,J}$: subregular solution model parameter
- $G^x_{I,J}$: excess free energy in the binary IJ at a normalized composition of $N_I/(N_I + N_J)$, i.e. $N_I + N_J < 1.0$
- $W(I,J)$: effective regular solution model parameter in the binary IJ at $N_I/(N_I + N_J)$.
- $G^x$: matrix representation of the sub-regular parameters belonging to a ternary, I = row number, J = column number.
- $G^x$: ternary excess free energy.

**Acknowledgement**—This paper is published with the permission of the Undersecretary, Department of Mines of New South Wales. Dr. E. SLANSKY made helpful suggestions to improve the manuscript.
Fig. 6. Calculated model spinodal for the ternary feldspar system using a subregular KOHLER solution with $W_{ij}$ (as indicated, in cal/mole) calculated at 1,000°C, 1 kb.

Fig. 7. Calculated model spinodal for the ternary feldspar system using a subregular KOHLER solution with temperature dependent $W_{ij}$ as indicated in the text. Data at 1 kb. An=1, Or=2, Ab=3.

REFERENCES


BARRON, L. M. (in prep.) Calculated immiscibility in the An-Or-Ab-Rb feldspar system at 1,000°C and 1 kb.


Appendix A. The spinodal equation for a KOHLER solution

The sequence that MEIJIRING (1950) followed in developing the spinodal equation for a ternary regular solution is applicable to a ternary KOHLER solution as well. The main step is that

\[
\frac{\partial^2 G}{\partial x \partial x} \left( \frac{\partial^2 G}{\partial y \partial y} \right) = \left( \frac{\partial^2 G}{\partial x \partial y} \right)^2 \quad \text{(A1)}
\]

defines the spinodal condition where \( x = N_1 \) and \( y = N_2 \). To apply this to a KOHLER solution we need only determine expressions for \( \frac{\partial^2 G}{\partial x \partial x}, \frac{\partial^2 G}{\partial y \partial y} \) and \( \frac{\partial^2 G}{\partial x \partial y} \). Since KOHLER’s model uses normalized binary compositions the following subsidiary relations will be needed.

With \( Z_{IJ} = N_I/(N_1 + N_J) \)

\[
\begin{array}{c|c|c|c}
I & J & \frac{\partial Z_{IJ}}{\partial N_1} & \frac{\partial Z_{IJ}}{\partial N_2} \\
1 & 2 & N_2/(N_1 + N_2) & -N_1/(N_1 + N_2)^2 \\
1 & 3 & 1/(1-N_2) & N_1/(1-N_2)^2 \\
2 & 3 & N_2/(1-N_2) & 1/(1-N_1) \\
\end{array}
\quad \text{(A2)}
\]

It can be shown that

\[
\frac{\partial Z_{IJ}}{\partial N_K} = -\frac{\partial Z_{IJ}}{\partial N_K} \quad \text{where } K = 1 \text{ or } 2. \quad \text{(A4)}
\]

KOHLER’s (1960) model for a ternary is expressed as

\[
G^x = (N_1 + N_2)^2 G^x_{12} + (1-N_2)^2 G^x_{13} + (1-N_1)^2 G^x_{23} \quad \text{(A5)}
\]

while \( G \equiv G^x + RT \sum_{i=1}^3 N_i \ln N_i \).

With \( \theta_{IJ} \equiv \frac{dG^x_{IJ}}{dZ_{IJ}} \) we arrive at

\[
\frac{\partial G}{\partial N_1} = 2(N_1 + N_2)G^x_{12} + N_2 \theta_{12} + (1-N_2) \theta_{13} - 2(1-N_1)G^x_{23} + N_2 \theta_{23} + RT \ln N_1 - \ln N_3 \quad \text{(A8)}
\]

so that with \( \theta'_{IJ} \equiv \frac{d^2G^x_{IJ}}{dZ_{IJ}^2} \) we arrive at

\[
\frac{\partial^2 G}{\partial N_1^2} = 2(G^x_{12} + G^x_{23}) + 2N_2 \left[ \theta_{12}/(N_1 + N_2) - \theta_{23}/(1-N_2) \right] + N_2^2 \left[ \theta'_{12}/(N_1 + N_2)^2 + \theta'_{13}/(1-N_2)^2 + \theta'_{23}/(1-N_1)^2 \right] + RT \left( 1/N_1 + 1/N_3 \right) \equiv A + RT \left( 1/N_1 + 1/N_3 \right) \quad \text{(A9)}
\]

The relation for \( d^2G/dN_2^2 \) is found to be

\[
\frac{\partial^2 G}{\partial N_2^2} = 2(G^x_{12} + G^x_{13}) - 2N_1 \theta_{12}/(N_2 + N_2) - 2N_1 \theta_{13}/(1-N_2) + N_1 \theta'_{12}/(N_1 + N_2)^2 + N_2 \theta'_{13}/(1-N_2)^2 + \theta'_{23}/(1-N_1) + RT \left( 1/N_2 + 1/N_3 \right) \equiv B + RT \left( 1/N_2 + 1/N_3 \right) \quad \text{(A10)}
\]

while that for the remaining term is

\[
\frac{\partial^2 G}{\partial N_1 \partial N_2} = 2G^x_{12} + (N_2 - N_1) \theta_{12}/(N_1 + N_2)^2 - \theta_{13}/(1-N_2) + N_1 \theta'_{12}/(N_1 + N_2)^2 + N_2 \theta'_{13}/(1-N_2) + \theta'_{23}/(1-N_1) + RT/N_3 \equiv C + RT/N_3 \quad \text{(A12)}
\]

A10, A11 and A12 are now combined according to (A1) which results in

\[
A1(RT)^2 + B1(RT) + C1 = 0 \quad \text{where} \quad (A13)
\]

\[
A1 \equiv 1/N_2^2 - (1/N_1 + 1/N_3) (1/N_2 + 1/N_3) \quad \text{(A14)}
\]

\[
B1 \equiv 2C/N_3 - A(1/N_1 + 1/N_3) - B(1/N_1 + 1/N_3) \quad \text{(A15)}
\]

\[
C1 \equiv (C - AB) \quad \text{(A16)}
\]

Equation (A13) is a quadratic so the solution is

\[
RT = \left[ -B1 \pm \sqrt{B1^2 - 4A1C1} \right] / 2A1 \quad \text{(A17)}
\]
To date the most positive values of $T$ have been found with the minus sign in front of the square root in (A17). These equations (A5 to A17) can be used with a subregular solution because

$$\theta'_{IJ} = W_{IJ} (2 - 6Z_{IJ}) + W_{IJ} (6 Z_{IJ} - 4)$$

while

$$\theta_{IJ} = \bar{U}^X_I - \bar{U}^X_J$$

where

$$\bar{U}^X_I = (Z_{JI})^2 [W_{IJ} - 2 (W_{JI} - W_{IJ}) Z_{IJ}]$$

after THOMPSON (1967).

The situation where the parameters $W$ have a temperature dependence may be handled in the following manner. Let $T$ be the temperature used to calculate the parameters $W_{IJ}$, $\theta'_{IJ}$ while $T_1$, $T_2$, $T_3$, ... represent the successive values of the calculated spinodal temperature at one fixed composition. The scheme $T = (T_n + T_{n-1})/2$ causes very rapid convergence (4-6 iterations; error ±0.5°) which to date is due to the fact that $T_n$ oscillates about the final resting point. This may not be a general pattern so that some caution is required in its future use.

A program, written in BASIC, calculates the spinodal for a KOHLER solution. Copies of the listing of this program are available upon request. The program is entitled QUATGP and has the additional ability to calculate ternary and quaternary binodals. The spinodal output from QUATGP is in a triangular print-out that can be laid on top of an equilateral triangle of 20cm side-length with 4-digit temperatures ($^\circ$C) overlying composition points at 0.05 mole fraction intervals. Contouring is done by hand. The print-out is in the order; component 3 in the left hand corner, component 2 in the right hand corner and component 1 at the apex which is pointing down.