

## RAPID PHASE DETERMINATION IN MULTIPLE-PHASE FLASH CALCULATIONS

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**Abstract**—A formulation of the equations which describe the behavior of systems which can form three phases is presented. The method can be extended to systems of more than three phases if desired. Key features of the method are: (1) rapid *a priori* determination of the number of phases actually present, based on a multi-phase generalization of the well-known bubble- and dew-point criteria; and (2) rapid solution of the equations once the number of phases has been determined. The method was developed for incorporation into a general purpose, modular flowsheet simulation system.

**Scope**—The work reported here was undertaken many years ago as part of an effort to implement a general capability to deal with three-phase systems in SPECS, the Shell Process Engineering Calculation System. In the mid-1960's, the late Professor Richard R. Hughes was manager of the Applied Mathematics Department and later of the Chemical Engineering Department at the Shell Development Company. He gave strong support to the development of a number of computer programs for process engineering computations. In particular, he was a strong early advocate of the development of a comprehensive flowsheet simulation system. Of his many contributions to Shell, SPECS has been the most enduring. It is with pleasure that the author submits this paper in his honor.

The main objective of this work was to develop a three-phase flash algorithm for incorporation into a general purpose, modular flowsheet simulation system. The requirements placed on such an algorithm were:

(1) since the simulator is modular and allows the engineer to specify any of a number of various methods for representing thermodynamic properties, the flash algorithm should not be tied to any specific method, but should be able to solve flash problems in terms of  $K$ -values supplied by any method. In the case of composition-dependent  $K$ -values, this will, of course, require iterative calculations;

(2) since flash calculations are performed literally tens of thousands of times in a moderately sized commercial simulation, the algorithm must be fast;

(3) since flash calculations are called under a wide variety of conditions, the algorithm must be very robust. By this we mean that it must solve the problem posed if at all possible and if not, must respond to the calling program in a way which suggests appropriate corrective action.

In considering item (2) it was realized that one large source of wasted computation time can result when a system which may have three-phases is considered under conditions at which only one or two are actually present. In such a case, it is desirable to recognize the presence of only one- or two-phases as quickly as possible, to allow the use of simplified algorithms. The major contribution of this work is such a procedure. In addition, the flash equations are formulated in such a way as to give insight into those characteristics which make for easy solution by the Newton-Raphson method.

**Conclusions and Significance**—The algorithms documented in this paper were installed in the Shell Process Engineering Calculation System in 1973. Since that time they have repeatedly proven to be fast, reliable and good citizens of a modular flowsheeting environment. The presence of such routines made possible the subsequent incorporation of a number of unit operations with the capability of dealing with multiple phases.

One limitation of the method is that an initial estimate of the composition of the second liquid-phase, if present, must be provided. In practice, a process engineer almost always knows which component in his slate will dominate a second liquid-phase. In the unit operation methods which we have installed in SPECS, we simply require the engineer to designate that component and assume that the second liquid-phase is pure in that component until modified by iterative recalculation of the compositions. In practice, this has proven to be a workable and reliable technique.

### INTRODUCTION

In recent years the subject of multiple phase flash calculations has received considerable attention. Early work by Osborne [1] described a method which was primarily oriented toward hand calculation and used direct substitution iteration. Another early paper by Deam and Maddox [2] suggested a technique by which the Newton-Raphson method could be applied to accelerate convergence. However, one

of the two simultaneous equations which must be solved in the method of Deam and Maddox is poorly suited for this technique, since it has two disjoint solutions in the domain of interest. The fact that it is possible to formulate flash equations in such a way is often not appreciated and even very recent papers have continued to propose equations which have multiple roots [3-4].

The traditional flash algorithm is derived from the thermodynamic condition that fugacity be matched

for each component in each phase. More recently, flash algorithms based on Gibbs free energy minimization have appeared [5-6]. It may be asserted that free energy minimization is superior to fugacity matching because the latter condition does not guarantee that the solution is in fact a global minimum. This distinction is more apparent than real. As a practical matter, Gibbs free energy is minimized by techniques which produce a set of equations exactly analogous to, but more complex than, those required to match fugacities. Solution of these equations guarantees only a stationary point and the issue of global minimization still requires further confirmation. For normal physical equilibrium calculations, not involving reactions, there appears to be no advantage and some penalty, for the use of free energy minimization. This assertion would seem to be supported by the conclusions of Ohanomah and Thompson [7], who conducted a comprehensive study of a variety of techniques for multi-phase equilibrium calculations and found free energy minimization not to be competitive.

There are several types of flash problems of interest to chemical engineers. The most frequently invoked in a flowsheet simulation is the isothermal, isobaric flash, called "Type VI" by Boston and Britt [8]. The overall system composition, temperature and pressure are specified and it is required to know the composition and amount of each separate phase. The flash equations will first be derived for this case and then extended to several other types of flash problems.

#### ISOTHERMAL-ISOBARIC FLASH

##### Development of the flash equations

The material balance for a three-phase flash is:

$$f_i = L_1 x_{i1} + L_2 x_{i2} + V y_i; \quad i = 1, 2, \dots, n. \quad (1)$$

We express the two liquid-phase mol fractions in terms of the vapor-phase mol fractions by means of the vapor-liquid equilibrium coefficients,  $K_{i1}$  and  $K_{i2}$ :

$$f_i = L_1 \frac{y_i}{K_{i1}} + L_2 \frac{y_i}{K_{i2}} + V y_i. \quad (2a)$$

This equation can be solved for the vapor phase mol fraction:

$$y_i = \frac{f_i K_{i1} K_{i2}}{V K_{i1} K_{i2} + L_1 K_{i2} + L_2 K_{i1}}. \quad (3a)$$

Alternately, all mol-fractions in equation (1) could be related to the mol-fraction in liquid-phase 1 or liquid-phase 2:

$$f_i = L_1 x_{i1} + L_2 \frac{K_{i1}}{K_{i2}} x_{i1} + V K_{i1} x_{i1}, \quad (2b)$$

$$f_i = L_1 \frac{K_{i2}}{K_{i1}} x_{i2} + L_2 x_{i2} + V K_{i2} x_{i2}. \quad (2c)$$

These equations then yield expressions for the mol-

fractions in the liquid-phases:

$$x_{i1} = \frac{f_i K_{i2}}{V K_{i1} K_{i2} + L_1 K_{i2} + L_2 K_{i1}}, \quad (3b)$$

$$x_{i2} = \frac{f_i K_{i1}}{V K_{i1} K_{i2} + L_1 K_{i2} + L_2 K_{i1}}. \quad (3c)$$

Equation (3a) may be summed over all components to yield:

$$1 = \sum_i \frac{f_i K_{i1} K_{i2}}{V K_{i1} K_{i2} + L_1 K_{i2} + L_2 K_{i1}} \quad (4)$$

By an overall material balance:

$$V = F - L_1 - L_2 \quad (5)$$

Inserting equation (5) into equation (4) and rearranging we have:

$$\begin{aligned} P_1(\psi_1, \psi_2) &= \sum_i \frac{Z_i K_{i1} K_{i2}}{K_{i1} K_{i2} + \psi_1 K_{i2}(1 - K_{i1}) + \psi_2 K_{i1}(1 - K_{i2})} - 1 \\ &= \sum_i \frac{Z_i [-\psi_1 K_{i2}(1 - K_{i1}) - \psi_2 K_{i1}(1 - K_{i2})]}{K_{i1} K_{i2} + \psi_1 K_{i2}(1 - K_{i1}) + \psi_2 K_{i1}(1 - K_{i2})} = 0. \end{aligned} \quad (6a)$$

Likewise, equations (3b) and (3c) become:

$$\begin{aligned} P_2(\psi_1, \psi_2) &= \sum_i \frac{Z_i [(1 - \psi_1) K_{i2}(1 - K_{i1}) - \psi_2 K_{i1}(1 - K_{i2})]}{K_{i1} K_{i2} + \psi_1 K_{i2}(1 - K_{i1}) + \psi_2 K_{i1}(1 - K_{i2})} = 0, \quad (6b) \\ P_3(\psi_1, \psi_2) &= \sum_i \frac{Z_i [-\psi_1 K_{i2}(1 - K_{i1}) + (1 - \psi_2) K_{i1}(1 - K_{i2})]}{K_{i1} K_{i2} + \psi_1 K_{i2}(1 - K_{i1}) + \psi_2 K_{i1}(1 - K_{i2})} = 0. \end{aligned} \quad (6c)$$

Equations (6a-c) constitute a system of three algebraic equations, each of which must be satisfied at the solution. Since there are only two independent variables, the phase ratios  $\psi_1$  and  $\psi_2$ , only two of the equations may be independent. Furthermore, none of these equations are really suitable for solution by a Newton-Raphson technique. To see why this is so, consider the function  $P_1(\psi_1, \psi_2)$ , which is pictured in Fig. 1. The domain of interest is the triangular region with vertices at (0, 0), (0, 1) and (1, 0).  $P_1(\psi_1, \psi_2)$  is

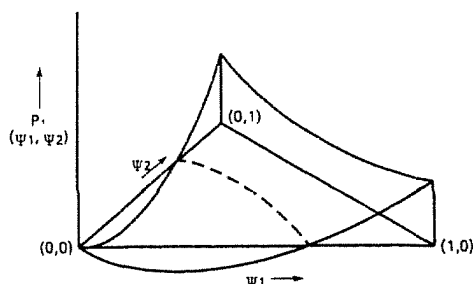


Fig. 1. The function  $P_1(\psi_1, \psi_2)$ .

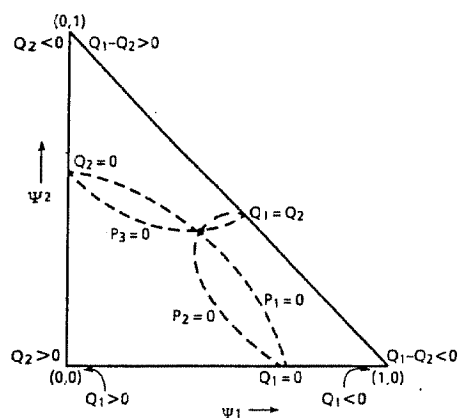


Fig. 2. Location of the zeros of  $P_1$ ,  $P_2$  and  $P_3$  for normal three-phase behavior.

zero along the dashed line, but the function also has a superfluous root at  $(0, 0)$  which is of no physical interest. The effect of this root is to cause the function to take a minimum value at some point along any ray originating at the origin. This causes trouble for root-finding techniques based on the gradient (e.g. Newton-Raphson) since these methods tend to force convergence toward either root, depending on the starting point. The functions  $P_2(\psi_1, \psi_2)$  and  $P_3(\psi_1, \psi_2)$  exhibit the same behavior as  $P_1(\psi_1, \psi_2)$  except that they have their superfluous roots at  $(1, 0)$  and  $(0, 1)$  respectively, instead of  $(0, 0)$ . Each also takes the value zero along a locus within the domain. Three such loci are thus defined, which must intersect at a common point representing the solution to the flash problem (Fig. 2).

Two independent functions which have properties more suitable for numerical solution can be derived from equations (6a-c). These are:

$$Q_1(\psi_1, \psi_2) = P_2(\psi_1, \psi_2) - P_1(\psi_1, \psi_2) \\ = \sum_i \frac{Z_i K_{i2}(1 - K_{i1})}{K_{i1}K_{i2} + \psi_1 K_{i2}(1 - K_{i1}) + \psi_2 K_{i1}(1 - K_{i2})} = 0, \quad (7a)$$

$$Q_2(\psi_1, \psi_2) = P_3(\psi_1, \psi_2) - P_1(\psi_1, \psi_2) \\ = \sum_i \frac{Z_i K_{i1}(1 - K_{i2})}{K_{i1}K_{i2} + \psi_1 K_{i2}(1 - K_{i1}) + \psi_2 K_{i1}(1 - K_{i2})} = 0. \quad (7b)$$

The  $P$ -functions can be written in terms of the  $Q$ -functions:

$$P_1(\psi_1, \psi_2) = -\psi_1 Q_1(\psi_1, \psi_2) \\ - \psi_2 Q_2(\psi_1, \psi_2), \quad (8a)$$

$$P_2(\psi_1, \psi_2) = (1 - \psi_1) Q_1(\psi_1, \psi_2) \\ - \psi_2 Q_2(\psi_1, \psi_2), \quad (8b)$$

$$P_3(\psi_1, \psi_2) = -\psi_1 Q_1(\psi_1, \psi_2) \\ + (1 - \psi_2) Q_2(\psi_1, \psi_2). \quad (8c)$$

Simultaneous solution of equation (7a, b) will yield the same values of  $\psi_1$  and  $\psi_2$  as simultaneous solution

of equation (6a-c). But the  $Q$ -functions are more suitable for iterative solution because they contain no superfluous roots in the domain of interest.

The two-phase equivalent of the  $Q$ -functions is well known, going back to Rachford and Rice [9]. These authors did not, however, examine the behavior of this function at the limiting cases of pure vapor or pure liquid-phases. Such an examination leads to simple and well-known criteria for the existence of two-phases based on bubble point and dew point calculations. The proper extension of the  $Q$ -functions to multiple-phases does not seem to be as widely appreciated. The algorithm proposed by Wu and Bishnoi [3] and the earlier algorithm of Deam and Maddox [2] corresponds to solving equations (7a) and (6c) of this work. Equation (6c), as has been discussed, has multiple roots. The intent of this paper is simply to show how the simple and well-known bubble- and dew-point criteria for two-phases can be extended to multiple-phase systems.

#### Tests for the existence of only two-phases

In many cases only one- or two-phases of a potentially three-phase system are present. A great deal of effort can be saved if the number and nature of the phases can be determined before a search for three-phases is begun. This was a clear finding of the work of Ohanmah and Thompson [7] and can be readily understood when it is appreciated that one- and two-phase systems are described by points along the boundaries of the three-phase domain. If the solution point is not known in advance to lie on the boundary, it will be approached gingerly by a general purpose three-phase algorithm, in order to avoid violating the constraint.

Algorithms for testing the existence of multiple-phases are included in various descriptions of Gibbs free energy minimization techniques such as those of Michelsen [6] and Shah [10]. A very elegant treatment of phase stability has been given by Van Dongen *et al.* [11], who studied the "material stability" of a phase, that is to say, its stability relative to two-phases of incrementally different composition. They show that the positive definiteness of the matrix of second derivatives of molar Gibbs free energy with respect to composition is a necessary and sufficient condition for stability in this sense. However, for practical engineering computations, the determination of material stability is of less significance than the determination of metastability, which is the propensity of a given phase to split into two or more phases which may differ widely in composition. Van Dongen *et al.* do not address this question, commenting only that, "The only way to check for this possibility is by making an extensive search."

The algorithm to be described here deals with the issue of phase metastability. It is based on the  $K$ -values supplied to the flash routine and does not require free energy computations. Of course, free

Table 1. Values of  $Q_1$ ,  $Q_2$  and  $Q_1 - Q_2$  at the vertices

$\psi_1$	$\psi_2$	$Q_1(\psi_1, \psi_2)$	$Q_2(\psi_1, \psi_2)$	$Q_1(\psi_1, \psi_2) - Q_2(\psi_1, \psi_2)$
0	0	$\sum_i \frac{Z_i}{K_{i1}} - 1$	$\sum_i \frac{Z_i}{K_{i2}} - 1$	$\sum_i \frac{Z_i}{K_{i1}} - \sum_i \frac{Z_i}{K_{i2}}$
1	0	$1 - \sum_i Z_i K_{i1}$	$\sum_i Z_i \frac{K_{i1}}{K_{i2}} - \sum_i Z_i K_{i1}$	$1 - \sum_i Z_i \frac{K_{i1}}{K_{i2}}$
0	1	$\sum_i Z_i \frac{K_{i2}}{K_{i1}} - \sum_i Z_i K_{i2}$	$1 - \sum_i Z_i K_{i2}$	$\sum_i Z_i \frac{K_{i2}}{K_{i1}} - 1$

energy calculation may have gone into the determination of the  $K$ -values themselves. The flash algorithm does not need to know how the  $K$ -values were calculated. Further, all phases are treated symmetrically, unlike the treatment of Shah, which presupposes the existence of vapor- and liquid-phase 1 and tests only the appearance of liquid-phase 2 using Gibbs free energy considerations. Fournier and Boston [12] extended the flash method of Boston and Britt to multiple liquid-phases, incorporating the method of Shah for testing phase stability.

The ultimate validity of the present method depends on the ability to estimate the composition of the phase whose stability is in question. This is true of the free energy methods as well. For practical engineering computations, the process engineer virtually always knows which component will dominate a second liquid-phase if one forms. It will, in fact, frequently be either water or a component added to the process for the specific purpose of creating such a phase. We have found that the method to be described below is suitably rigorous and entirely satisfactory for general purpose process engineering calculations, and that a suitable starting point can generally be obtained by assuming that the second liquid-phase, if one exists, is pure in the identified dominant component. It must be stressed, however, that this is not a universally applicable procedure. When  $K$ -values are highly composition dependent it is possible that the system composition will be found to be stable when tested against a proposed pure-phase, when in fact another suitably composed liquid-phase will separate. In such a case, the criteria presented here work properly when the proposed incipient-phase compositions are correct. But the criteria do not help in the selection of trial compositions. This is a general problem with any phase stability determination method. It has been addressed by Michelsen [6] and by Gautam and Seider [5] in the context of Gibbs free energy minimizing algorithms. Their methods of selecting trial-phase compositions can just as well be used in conjunction with the present method for testing phase-stability and completing flash calculations.

In order to understand the behavior of three-phase systems, it is useful to evaluate the functions  $Q_1(\psi_1, \psi_2)$  and  $Q_2(\psi_1, \psi_2)$  at the vertices and along the edges of the triangular domain of Fig. 2. Such evaluations at the vertices are shown in Table 1 for

$Q_1$ ,  $Q_2$  and  $Q_1 - Q_2$ . Under normal circumstances, in the three-phase region, it is found that:

$$\sum_i Z_i K_{i1} > 1, \quad (9a)$$

$$\sum_i \frac{Z_i}{K_{i1}} > 1. \quad (9b)$$

These relations are not inviolate, but if they are not satisfied vapor- and liquid-phase 1 cannot coexist in the absence of a second liquid-phase and they may be considered normal. It is mathematically impossible for both

$$\sum_i Z_i K_{i1} \quad \text{and} \quad \sum_i \frac{Z_i}{K_{i1}}$$

to be less than unity. Similar remarks apply to the relations:

$$\sum_i Z_i K_{i2} > 1, \quad (9c)$$

$$\sum_i \frac{Z_i}{K_{i2}} > 1, \quad (9d)$$

and to

$$\sum_i Z_i \frac{K_{i1}}{K_{i2}} > 1, \quad (9e)$$

$$\sum_i Z_i \frac{K_{i2}}{K_{i1}} > 1. \quad (9f)$$

The relations in inequalities (9a-f) lead to the normal behavior of the functions  $Q_1$ ,  $Q_2$  and  $Q_1 - Q_2$  shown in Fig. 2. The function  $Q_1(0, 0)$  is normally positive and  $Q_1(1, 0)$  is normally negative.  $Q_1$  must then be zero somewhere along the  $\psi_1$ -axis. Equations (8a) and (8b) indicate that at that point  $P_1(\psi_1, 0)$  and  $P_2(\psi_1, 0)$  are zero as well. Similar considerations govern the behavior of  $Q_2(0, \psi_2)$  along the  $\psi_2$ -axis and of  $Q_1(\psi_1, 1 - \psi_1) - Q_2(\psi_1, 1 - \psi_1)$  along the diagonal edge.

Consider a system described by the point  $Q_1(\psi_1, 0) = 0$  along the  $\psi_1$ -axis as shown in Fig. 2. At this point  $P_3(\psi_1, 0) = Q_2(\psi_1, 0) > 0$ . There will be a tendency for such a system to form a second liquid-phase, thus moving toward the equilibrium point within the domain. Suppose, however, that  $P_3(\psi_1, 0) = Q_2(\psi_1, 0)$  were less than zero at this point. This could happen for example, if the dotted line showing the zeros of the  $P$ -functions were as shown in Fig. 3. In this case there would be no tendency for

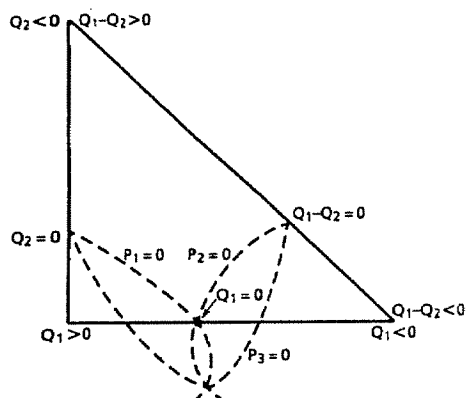


Fig. 3. Location of the zeros of  $P_1$ ,  $P_2$  and  $P_3$  for two-phase behavior.

a second liquid-phase to form. It appears then that a valid test for the existence of only two-phases is that  $Q_1(\psi_1, 0) = 0$  have a solution in the region  $0 < \psi_1 < 1$  and that  $Q_2(\psi_1, 0) < 0$  at that point. In this case the two phases are vapor- and liquid-phase 1. Similar analyses along the other edges of the triangular domain can be used to determine the existence of other combinations of two-phases.

The criteria for the existence of two-phases can be summarized as follows:

(i) vapor- and liquid-phase 1:

$$\sum_i \frac{Z_i}{K_{i1}} > 1; \quad \sum_i Z_i K_{i1} > 1$$

and  $Q_2(\psi_1, 0) < 0$  at the root of  $Q_1(\psi_1, 0) = 0$ ;

(ii) vapor- and liquid-phase 2:

$$\sum_i \frac{Z_i}{K_{i2}} > 1; \quad \sum_i Z_i K_{i2} > 1$$

and  $Q_1(0, \psi_2) < 0$  at the root of  $Q_2(0, \psi_2) = 0$ ;

(iii) liquid-phase 1 and liquid-phase 2:

$$\sum_i Z_i \frac{K_{i1}}{K_{i2}} > 1; \quad \sum_i Z_i \frac{K_{i2}}{K_{i1}} > 1$$

and  $Q_1(\psi_1, 1 - \psi_1) > 0$  [or  $Q_2(\psi_1, 1 - \psi_1) > 0$ ] at the root of  $Q_1(\psi_1, 1 - \psi_1) - Q_2(\psi_1, 1 - \psi_1) = 0$  along the diagonal edge.

One might wonder whether under certain pathological conditions more than one of the above two-phase tests may be satisfied at the same time. In fact, this is not possible. A proof of this assertion is given in the Appendix.

In order to evaluate these criteria, a 1-D iterative search procedure is necessary along each boundary under normal circumstances. Such a search adds time to the initial set up phase of the problem of determining the solution of a three-phase flash. The extra time is well spent, however, when the potential benefit is a determination that a three-phase flash calculation is not needed. Moreover, once it is determined that

only two-phases are present, the phase ratios are already at hand. It remains only to calculate phase compositions from equations (3a-c) and the problem has been solved.

#### Tests for the existence of only one-phase

If inequality (9a) is violated there is no tendency for a liquid-phase 1 with the composition of the feed to form a vapor-phase. Likewise, if inequality (9e) is violated, there is no tendency for such a liquid-phase to form a second liquid-phase. It appears then that the simultaneous violation of inequalities (9a) and (9e) is an adequate test for the existence of liquid-phase 1 alone. This corresponds to raising the value of  $Q_1(1, 0)$  and of  $Q_1(1, 0) - Q_2(1, 0)$  until both are greater than zero. The point  $Q_1 = 0$  on the  $\psi_1$ -axis (Fig. 3) moves to and beyond the (1,0) vertex as does the point  $Q_1 - Q_2 = 0$  along the diagonal.

Similar tests apply for the existence of a single vapor-phase or liquid-phase 2. These can be summarized as follows:

(i) vapor-phase alone:

$$\sum_i \frac{Z_i}{K_{i1}} < 1 \quad \text{and} \quad \sum_i \frac{Z_i}{K_{i2}} < 1;$$

(ii) liquid-phase 1 alone:

$$\sum_i Z_i K_{i1} < 1 \quad \text{and} \quad \sum_i Z_i \frac{K_{i1}}{K_{i2}} < 1;$$

(iii) liquid-phase 2 alone:

$$\sum_i Z_i K_{i2} < 1 \quad \text{and} \quad \sum_i Z_i \frac{K_{i2}}{K_{i1}} < 1.$$

Since tests for the existence of a single phase can be performed without iterative calculations, they should be applied before the two-phase tests of the previous sections. The impossibility of simultaneous violation of inequalities (9a) and (9b) assures that tests (i) and (ii) will not both be passed. Similar reasoning precludes simultaneous satisfaction of any other pair of the above tests.

Two other impossible combinations of events may be noted. It is not possible to have the simultaneous occurrence of:

$$\sum_i Z_i K_{i1} < 1; \quad \sum_i \frac{Z_i K_{i2}}{K_{i1}} < 1; \quad \sum_i \frac{Z_i}{K_{i2}} < 1.$$

This would be equivalent to a vapor condensing to form liquid-phase 1, which moves over to liquid-phase 2, which vaporizes. Such a circular process is clearly not possible. By similar reasoning, it is impossible to have the simultaneous occurrence of:

$$\sum_i \frac{Z_i}{K_{i1}} < 1; \quad \sum_i Z_i K_{i2} < 1; \quad \sum_i Z_i \frac{K_{i1}}{K_{i2}} < 1.$$

It should be noted that compositions for all three phases should be calculated using equations (3a-c) even though only one or two phases are present. Molar fractions for nonexistent phases will sum to less than

unity and should be normalized. The reason for this is that  $K$ -values in a system which can form three phases are invariably composition dependent. This means that when convergence is achieved with a given set of  $K$ -values, they must be reevaluated at the newfound compositions of the phases. A new three-phase flash is performed and this procedure is iterated until composition and  $K$ -values converge. The calculation of a  $K$ -value ordinarily requires the composition of both liquid- and vapor-phases so these must be provided even if one or both of the phases do not exist. The normalized composition in this case may be construed as the composition of the first incremental amount of the phase that could form. As noted above, the computation may be started by assuming that the second liquid-phase consists purely of a dominant component identified by the process engineer. However, in highly non-ideal systems, a more elaborate procedure for selecting trial phase compositions may be necessary.

It may be noted that the  $\psi_1 = 0$  and  $\psi_2 = 0$  axes in Fig. 2 represent identical systems in the sense that only one liquid-phase is present and the  $K$ -values are determined solely on the basis of the composition of that phase. It is somewhat immaterial whether one calls this "liquid-phase 1" or "liquid-phase 2". The difference between these two points is somewhat notional and depends on the *a priori* labels that the process engineer applies to the phases. In a system where water and hydrocarbons are jointly present, for example, it would be customary to think of a largely aqueous phase as the "second liquid-phase", even though in some calculations, such as a sour water stripper or an acid gas absorber, a hydrocarbon "first liquid-phase" may not exist. The practical difference between these axes is then the trial-phase composition that one would propose for an alternate liquid-phase. Whereas the  $K$ -values between an existing liquid-phase and vapor are determined by the composition of that phase, the  $Q$ -functions also require  $K$ -values for a proposed additional phase, the trial composition of which is suggested by the label which is applied to it.

#### Solution of a three-phase flash

Once it has been determined that three phases are present, a 2-D search must be performed for the values of  $\psi_1$  and  $\psi_2$  which cause equations (7a, b) to be satisfied. If the flash is being performed with recalculated  $K$ -values from a previously converged solution, the previous values of  $\psi_1$  and  $\psi_2$  are good starting estimates. Otherwise, reasonable starting values can be obtained from the search for two phases. Suppose, for example, that it was determined that  $Q_1(\psi_1, 0) = 0$  had a root in the region  $0 < \psi_1 < 1$  and that  $Q_2(\psi_1, 0) > 0$  at that root. Then  $(\psi_1, 0)$  is a reasonable starting point. It may be that  $Q_1(\psi_1, 0) = 0$  has no root along the edge of the domain, but for at least one of the two-phase tests a root will exist along an edge. Any combination of

violations of the inequalities (9a-f) which might preclude this has been previously declared to be impossible or else leads to a single phase system.

The Newton-Raphson iteration procedure can be used to search for the solution. The required partial derivatives of  $Q_1$  and  $Q_2$  with respect to  $\psi_1$  and  $\psi_2$  are:

$$\frac{\partial Q_1}{\partial \psi_1} = \sum_i \frac{-Z_i K_{i2}^2 (1 - K_{i1})^2}{[K_{i1} K_{i2} + \psi_1 K_{i2} (1 - K_{i1}) + \psi_2 K_{i1} (1 - K_{i2})]^2}, \quad (10a)$$

$$\frac{\partial Q_1}{\partial \psi_2} = \frac{\partial Q_2}{\partial \psi_1} = \sum_i \frac{-Z_i K_{i1} K_{i2} (1 - K_{i1}) (1 - K_{i2})}{[K_{i1} K_{i2} + \psi_1 K_{i2} (1 - K_{i1}) + \psi_2 K_{i1} (1 - K_{i2})]^2}, \quad (10b)$$

$$\frac{\partial Q_2}{\partial \psi_2} = \sum_i \frac{-Z_i K_{i1}^2 (1 - K_{i2})^2}{[K_{i1} K_{i2} + \psi_1 K_{i2} (1 - K_{i1}) + \psi_2 K_{i1} (1 - K_{i2})]^2}. \quad (10c)$$

Notice that  $\partial Q_1 / \partial \psi_1 < 0$  and  $\partial Q_2 / \partial \psi_2 < 0$ . This property is useful in establishing the convergence of the Newton-Raphson procedure to a unique solution. The solution procedure consists of finding successive estimates of the root by the iterative application of:

$$\begin{aligned} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}_{M+1} &= \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}_M - \begin{pmatrix} \frac{\partial Q_1}{\partial \psi_1} & \frac{\partial Q_1}{\partial \psi_2} \\ \frac{\partial Q_2}{\partial \psi_1} & \frac{\partial Q_2}{\partial \psi_2} \end{pmatrix}_M^{-1} \cdot \begin{pmatrix} Q_1 \\ Q_2 \end{pmatrix}_M \\ &= \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}_M - \frac{1}{D} \begin{pmatrix} \frac{\partial Q_2}{\partial \psi_2} & -\frac{\partial Q_1}{\partial \psi_2} \\ -\frac{\partial Q_2}{\partial \psi_1} & \frac{\partial Q_1}{\partial \psi_1} \end{pmatrix}_M \times \begin{pmatrix} Q_1 \\ Q_2 \end{pmatrix}_M, \quad (11) \end{aligned}$$

where  $D$  is the determinant of the Jacobian matrix:

$$D = \frac{\partial Q_1}{\partial \psi_1} \frac{\partial Q_2}{\partial \psi_2} - \frac{\partial Q_1}{\partial \psi_2} \frac{\partial Q_2}{\partial \psi_1}. \quad (12)$$

Convergence is declared when  $Q_1$  and  $Q_2$  are zero to within tolerance.

#### ISOTHERMAL FLASH AT SPECIFIED LIQUID FRACTION

This is the flash of Type IV as classified by Boston and Britt. In this type of flash, one wants to calculate the pressure required to achieve a specified degree of liquefaction at a given temperature. The relative amount and compositions of the two liquid-phases, if two form, are also unknown. In this case, the single-phase system is ruled out when the specified liquid fraction is between zero and unity.

In designing an algorithm to perform a flash calculation, it is well worthwhile to structure the calculation in such a way as to minimize the number of times a separate routine must be called to recalculate  $K$ -values. For the isothermal flash (preceding section) the dependence of  $K$ -value on phase

compositions is ignored while the program is searching for the correct values of  $\psi_1$  and  $\psi_2$  and is only included by means of an "outer loop" in which  $K$ -values are recalculated at new, converged phase compositions. In the problem at hand, however, we can make a good approximation to the dependence of the  $K$ -values on one of the problem variables, the pressure and can therefore greatly improve the efficiency of the convergence procedure. Assuming that we have starting  $K$ -values calculated at some pressure  $P^*$ , this approximation is:

$$K_i(P) = K_i(P^*) \frac{P^*}{P}. \quad (13)$$

The independent variables for this problem are  $\psi_1$  and  $P$  rather than  $\psi_1$  and  $\psi_2$  since  $\psi_2 = \psi - \psi_1$ , hence is no longer independent. Substituting equation (13) into equations (7a, b) and with appropriate changes in notation, we have:

$$Q_1(\psi, P) = \sum_i \frac{Z_i \left( K_{i2} - K_{i1} K_{i2} \frac{P^*}{P} \right)}{\psi_1 K_{i2} + (\psi - \psi_1) K_{i1}} + (1 - \psi) K_{i1} K_{i2} \frac{P^*}{P} \quad (14a)$$

$$Q_2(\psi_1, P) = \sum_i \frac{Z_i \left( K_{i1} - K_{i1} K_{i2} \frac{P^*}{P} \right)}{\psi_1 K_{i2} + (\psi - \psi_1) K_{i1}} + (1 - \psi) K_{i1} K_{i2} \frac{P^*}{P} \quad (14b)$$

A diagram of typical behavior of the zeros of  $Q_1$  and  $Q_2$  is shown in Fig. 4a for a three-phase system. A typical diagram for the case in which the second liquid-phase does not form is shown in Fig. 4b. This figure is analogous to Fig. 3 and comparison shows that when the intersection of  $Q_1 = 0$  and  $Q_2 = 0$  falls above the line  $\psi_1 = \psi$ , then the system is described by the intersection of  $Q_1 = 0$  with the line  $\psi_1 = \psi$ . Likewise it is easily shown that when the intersection of  $Q_1 = 0$  and  $Q_2 = 0$  falls below the line  $\psi_1 = 0$ , the system is described by the intersection of  $Q_2 = 0$  with  $\psi_1 = 0$ .

By comparison of Figs 4a and 4b, it is seen that if  $Q_2 < 0$  at the intersection of  $Q_1 = 0$  and  $\psi_1 = \psi$  [i.e. at the zero of  $Q_1(\psi, P)$ ] then there is no liquid-phase 2. Likewise, it is readily shown that if  $Q_1 < 0$  at the zero of  $Q_2(0, P)$  then there is no liquid-phase 1. If neither of these conditions occur, the system has all three possible phases.

The criteria for two-phase behavior can be summarized as follows:

- (i) vapor- and liquid-phase 1:  
 $Q_2(\psi, P) < 0$  at the root ( $P$  variable) of  $Q_1(\psi, P) = 0$ ;
- (ii) vapor- and liquid-phase 2:  
 $Q_1(0, P) < 0$  at the root of  $Q_2(0, P) = 0$ .

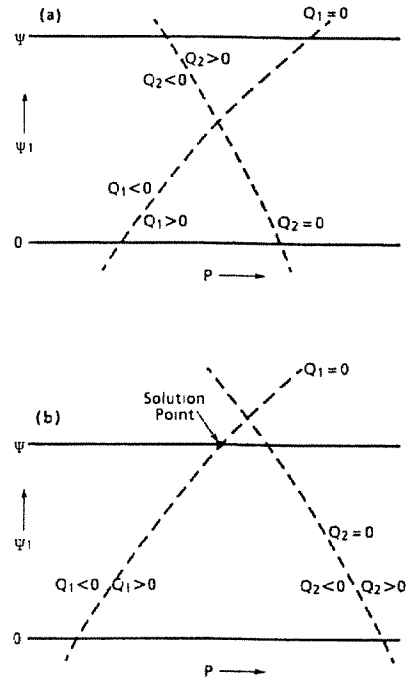


Fig. 4. (a) Zeros of  $Q_1(\psi_1, P)$  and  $Q_2(\psi_1, P)$  for a typical three-phase behavior; (b) zeros of  $Q_1(\psi_1, P)$  and  $Q_2(\psi_1, P)$  for two-phase behavior (no liquid-phase two).

If neither of the above tests for two-phase behavior are passed, the solution lies in the three-phase region and can be found using the Newton-Raphson method. The derivatives needed for the Jacobian matrix are:

$$\frac{\partial Q_1}{\partial P} = \frac{P^*}{P^2} \sum_i \frac{Z_i K_{i1} K_{i2} [K_{i2} + (\psi - \psi_1)(K_{i1} - K_{i2})]}{\left[ \psi_1 K_{i2} + (\psi - \psi_1) K_{i1} + (1 - \psi) K_{i1} K_{i2} \frac{P^*}{P} \right]^2}, \quad (15a)$$

$$\frac{\partial Q_2}{\partial P} = \frac{P^*}{P^2} \sum_i \frac{Z_i K_{i1} K_{i2} [K_{i1} + \psi_1(K_{i2} - K_{i1})]}{\left[ \psi_1 K_{i2} + (\psi - \psi_1) K_{i1} + (1 - \psi) K_{i1} K_{i2} \frac{P^*}{P} \right]^2}, \quad (15b)$$

$$\frac{\partial Q_1}{\partial \psi_1} = \sum_i \frac{-Z_i \left( K_{i2} - K_{i1} K_{i2} \frac{P^*}{P} \right) (K_{i2} - K_{i1})}{\left[ \psi_1 K_{i2} + (\psi - \psi_1) K_{i1} + (1 - \psi) K_{i1} K_{i2} \frac{P^*}{P} \right]^2}, \quad (15c)$$

$$\frac{\partial Q_2}{\partial \psi_1} = \sum_i \frac{-Z_i \left( K_{i1} - K_{i1} K_{i2} \frac{P^*}{P} \right) (K_{i2} - K_{i1})}{\left[ \psi_1 K_{i2} + (\psi - \psi_1) K_{i1} + (1 - \psi) K_{i1} K_{i2} \frac{P^*}{P} \right]^2}. \quad (15d)$$

These derivatives are used in a procedure entirely analogous to equations (ii) and (i2) to generate updated estimates of  $\psi_1$  and  $P$ . The procedure is iterated to convergence. At the converged condition, the  $K$ -values are recalculated at the new pressure and phase composition and the entire analysis is repeated. This continues until the difference between successive converged solutions is within the desired tolerance.

#### ISOBARIC FLASH AT SPECIFIED LIQUID FRACTION

This is the flash of Type V as classified by Boston and Britt. In this type of flash, one wants to calculate the temperature required to achieve a specified degree of liquefaction at a given pressure. The relative amounts and compositions of the two liquid-phases, if two form, are also unknown. As in the previous case, the single-phase system is ruled out when the specified liquid fraction is between zero and unity.

The problem is very similar to that in the previous section, except that useful approximations to the temperature dependence of the  $K$ -values may be more complex than the pressure dependence approximated in equation (13). A diagram of the typical behavior of the zeros of  $Q_1(\psi_1, T)$  and  $Q_2(\psi_1, T)$  is shown in Fig. 5a for a system that will form three phases. A system in which liquid-phase 2 will not form is shown in Fig. 5b. It should be noted that the intersection of the line  $Q_1 = 0$  and  $Q_2 = 0$  is also the intersection of the lines  $Q_1 + Q_2 = 0$  and  $Q_1 - Q_2 = 0$ . This obvious feature can be used to advantage in

searching for the intersection point when the dependence of these latter functions on  $T$  and  $\psi$  is as suggested in Fig. 5.

In order to test for two-phase behavior, the sign of  $Q_1(\psi, T) - Q_2(\psi, T)$  is tested. If it is found that  $Q_1(\psi, T) - Q_2(\psi, T) > 0$ , clearly the line  $Q_1 - Q_2 = 0$  lies above the line  $\psi_1 = \psi$  at that temperature. The working hypothesis is made that liquid-phase 2 does not form, and the algorithm begins a search for the point  $Q_1(\psi, T) = 0$ , which would yield the solution in this case. As long as  $Q_1(\psi, T) - Q_2(\psi, T) > 0$ , the algorithm stays with its hypothesis until convergence is obtained. But if, during the search, a temperature is encountered at which  $Q_1(\psi, T) - Q_2(\psi, T) < 0$ , the hypothesis is dropped and the algorithm resumes its search for a three-phase solution. Likewise, when the condition  $Q_1(0, T) - Q_2(0, T) < 0$  is encountered at any temperature, the algorithm begins to search for the temperature at which  $Q_2(0, T) = 0$  and similar reasoning is applied.

#### EXTENSION TO MORE THAN THREE PHASES

The foregoing analysis is readily extended to systems which may form more than three phases. We consider a system which may form  $N$  phases, a vapor phase and  $N - 1$  condensed phases. Then a generalization of the analysis leading up to equation (6a) leads to:

$$P_1(\psi_1, \dots, \psi_{N-1}) = \sum_i \frac{-Z_i \sum_{k=1}^{N-1} \psi_k \left( \frac{1}{K_{ik}} - 1 \right)}{1 + \sum_{k=1}^{N-1} \psi_k \left( \frac{1}{K_{ik}} - 1 \right)} \quad (16a)$$

Likewise, equation (6b, c) are generalized to:

$$P_{j+1}(\psi_1, \dots, \psi_{N-1}) = \sum_i \frac{Z_i \left[ \frac{1}{K_{ij}} - 1 - \sum_{k=1}^{N-1} \psi_k \left( \frac{1}{K_{ik}} - 1 \right) \right]}{1 + \sum_{k=1}^{N-1} \psi_k \left( \frac{1}{K_{ik}} - 1 \right)} \quad (16b)$$

Then the  $Q$ -functions defined in equation (7a, b) are generalized to:

$$Q_j(\psi_1, \dots, \psi_{N-1}) = \sum_i \frac{Z_i \left( \frac{1}{K_{ij}} - 1 \right)}{1 + \sum_{k=1}^{N-1} \psi_k \left( \frac{1}{K_{ik}} - 1 \right)} \quad (17)$$

It is straightforward from this point to extend the Newton-Raphson algorithm defined in equations (10)–(12) to higher dimensionality.

The progressive determination of the number of phases actually present proceeds along similar lines. The triangular region of Figs 1–3 becomes a polyhedron in three or more dimensions. The vertices are examined first to test for single-phase behavior. Then the edges are tested for two-phase behavior, the faces are tested for three-phase behavior, etc. The geometrical representation may become increasingly

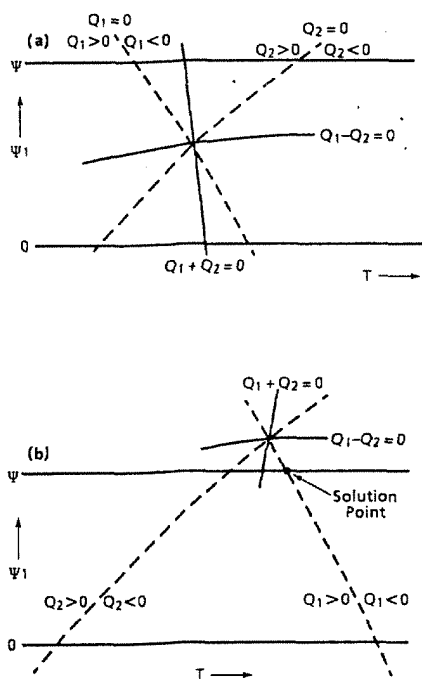


Fig. 5. (a) Zeros of  $Q_1(\psi_1, T)$  and  $Q_2(\psi_1, T)$  for a typical three-phase behavior; (b) zeros of  $Q_1(\psi_1, T)$  and  $Q_1(\psi_1, T)$  for two-phase behavior (no liquid-phase two).



Table 2. Sample flash calculations

	Feed Composition					
	Number	Name	Mol			
	1	Ethane	100			
	2	<i>n</i> -octane	300			
	3	Water	300			
Atmospheric pressure						

abstract as the dimensionality increases, but if the principles of the analysis are understood, then the reduction to computation is straightforward.

#### EXAMPLE CALCULATION

As a simple example of how the criteria are exploited, consider the isothermal flash of a three-component mixture of: (1) ethane (100 mol); *n*-octane (300 mol); and (3) water (300 mol) at atmospheric pressure and 195°F, using *K*-values calculated by the Redlich-Kwong-Soave equation of state method. The initially estimated *K*-values and the phase stability criteria evaluated from them are given in Table 2. None of the criteria for a single-phase solution are satisfied. However, examination of the summations suggests that the system may be two-phase vapor/liquid 1 or liquid 1/liquid 2. The root of  $Q_1(\psi_1, 0) = 0$  is found at  $\psi_1 = 0.141$ , and at that point  $Q_2(\psi_1, 0) = -0.287$ , so the criteria for a two-phase, vapor/liquid 1 system are satisfied. Correspondingly, if we examine further the criterion for a liquid 1/liquid 2 system, we find that the root of  $Q_1(\psi_1, 1 - \psi_1) - Q_2(\psi_1, 1 - \psi_1) = 0$  is found at

$\psi_1 = 0.569$ , and at this point  $Q_1(\psi_1, 1 - \psi_1) = Q_2(\psi_1, 1 - \psi_1) = -30.4$ , so this two-phase criterion is not satisfied. From the newly calculated phase compositions we recalculate *K*-values and repeat the process, which converges in five iterations. In each case two-phase behavior is predicted, and the ultimately converged solution is a two-phase solution. Note that after the first, ideal, estimate, the *K*-values are not very composition dependent and this contributes to rapid convergence and to the same phase behavior at every step of the iteration. For more non-ideal thermodynamic behavior, the *K*-values would be expected to change more from iteration to iteration, convergence would not be as rapid and the calculation may even wander back and forth between two-phase and three-phase regions. Techniques for accelerating convergence of flash calculations of highly non-ideal mixtures are known, but are not the subject of this paper.

If we repeat the above sequence of calculations at a lower temperature of 175°F, we find convergence in four iterations. At no time do the *K*-value criteria predict that one-phase or two-phase behavior will occur and the converged solution is indeed a three-phase mixture.

## NOMENCLATURE

- $\mathbf{A}, \mathbf{B}$  = Vectors with elements  $A_i$  and  $B_i$  defined by equations (A4) and (A5)  
 $D$  = Determinant of the Jacobian matrix, equations (12) and (A2)  
 $d_i$  = Defined by equation (A3)  
 $F$  = Total moles of feed to the flash  
 $f_i$  = Mol of component  $i$  in feed to flash  
 $K_{ij}$  = Vapor/liquid equilibrium coefficient for component  $i$  and liquid phase  $j$   
 $L_j$  = Mol of liquid phase  $j$   
 $N$  = Number of phases  
 $P$  = Pressure  
 $P^*$  = Reference pressure for  $K$ -value calculation  
 $P_j$  = Functions defined by equation (6a-c)  
 $Q_j$  = Functions defined by equation (7a, b)  
 $T$  = Temperature  
 $V$  = Mol of vapor phase  
 $x_{ij}$  = Mol fraction of component  $i$  the liquid phase  $j$   
 $y_i$  = Mol fraction of component  $i$  in vapor phase  
 $Z_i$  = Mol fraction of component  $i$  in feed  
 $\psi$  = Degree of liquefaction  $[(L_1 + L_2)/F]$   
 $\psi_j$  = Fraction of feed in liquid phase  $j$  ( $=L_j/F$ )  
 $N$  = Number of phases

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## APPENDIX

## Uniqueness of a Two-Phase Solution

The purpose of this appendix is to demonstrate that it is impossible that more than one test for a two-phase solution be satisfied. To show this, we will resort to a geometrical

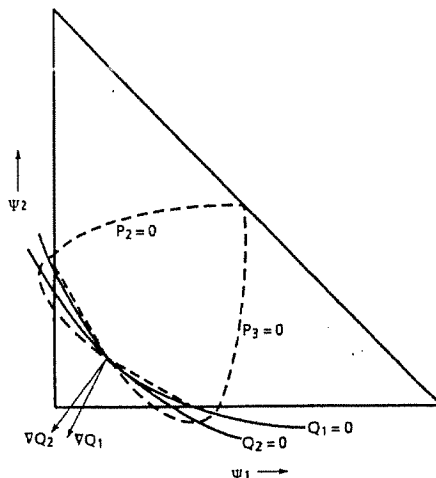


Fig. A1. Trajectories of the zeros of the  $P$  and  $Q$  functions for multiple two-phase solutions.

proof. Fig. A1 shows the type of trajectories for the zeros of the  $P$ -functions that would appear if two tests for two-phase behavior could be passed. In this case, coexistence of vapor- and liquid-phase 1 is found by one test and of vapor- and liquid-phase 2 by the other test.

Also shown in Fig. A1 are the trajectories for the zeros of the  $Q$ -functions. Using equation (8a-c) it is readily seen that  $Q_1 > 0$  at the lower intersection of the  $P_2 = 0$  trajectory with the  $\psi_2$ -axis and  $Q_1 < 0$  at the point  $Q_2 = 0$  along the axis. Therefore, the  $Q_1 = 0$  trajectory must intersect the  $\psi_2$ -axis as shown. Likewise, the  $Q_2 = 0$  trajectory must intersect the  $\psi_1$ -axis between the leftmost intersection of the  $P_3 = 0$  trajectory and the point  $Q_1 = 0$ . The trajectories of  $Q_1 = 0$  and  $Q_2 = 0$  must therefore intersect in the triangular domain. At the intersection (which would correspond to the solution of a three-phase flash) the gradients of  $Q_1$  and  $Q_2$  are oriented such that  $\nabla Q_1 \times \nabla Q_2 < 0$  in a right-handed Cartesian coordinate system.

A similar analysis of the trajectories of  $Q_1 = 0$  and  $Q_2 = 0$  for the case of a three-phase system (Fig. 2) or a system satisfying only one of the two phase criteria (Fig. 3) shows that at their intersection  $\nabla Q_1 \times \nabla Q_2 > 0$ . If we can demonstrate that the condition  $\nabla Q_1 \times \nabla Q_2 < 0$  is impossible, then our contention will be proved that at most one two-phase criterion can be satisfied. The cross product of the gradient is given by:

$$\nabla Q_1 \times \nabla Q_2 = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ \frac{\partial Q_1}{\partial \psi_1} & \frac{\partial Q_1}{\partial \psi_2} & 0 \\ \frac{\partial Q_2}{\partial \psi_1} & \frac{\partial Q_2}{\partial \psi_2} & 0 \end{vmatrix} = D\hat{k} \quad (\text{A1})$$

where  $\hat{i}$ ,  $\hat{j}$  and  $\hat{k}$  form a right-hand system of orthogonal vectors, and  $D$  is the determinant of the Jacobian matrix defined in equation (12). If we substitute equation (10a-c) into equation (12) we obtain:

$$D = \sum_i \frac{Z_i K_{i1}^2 (1 - K_{i1})^2}{d_i^2} \sum_i \frac{Z_i K_{i2}^2 (1 - K_{i2})^2}{d_i^2} - \left[ \sum_i \frac{Z_i K_{i1} K_{i2} (1 - K_{i1}) (1 - K_{i2})}{d_i^2} \right]^2 \quad (\text{A2})$$

where

$$d_i = K_{i1} K_{i2} + \psi_1 K_{i2} (1 - K_{i1}) + \psi_2 K_{i1} (1 - K_{i2}). \quad (\text{A3})$$

Now we define two  $N$ -dimensional vectors  $\mathbf{A}$  and  $\mathbf{B}$  with

elements  $\mathbf{A}_i$  and  $\mathbf{B}_i$  as follows:

$$\mathbf{A}_i = K_n(1 - K_n) \frac{\sqrt{Z_i}}{d_i},$$

$$\mathbf{B}_i = K_n(1 - K_n) \frac{\sqrt{Z_i}}{d_i}.$$

Then equation (A2) is equivalent to:

$$(A4) \quad D = |\mathbf{A}|^2 |\mathbf{B}|^2 - |\mathbf{A} \cdot \mathbf{B}|^2 \geq 0, \quad (A6)$$

(A5) the final result is that  $D \geq 0$  being proved by the Schwartz inequality. By equation (A1) this establishes the impossibility of  $\nabla Q_1 \times \nabla Q_2 < 0$ , which proves that at most one two-phase criterion can be satisfied.