

# A GENERAL EQUILIBRIUM CRITERION FOR AN ISOBARIC-ISOTHERMAL MODEL OF A CHEMICAL SYSTEM\*

Yu. V. Shvarov  
Moscow University

The inadequacy of existing criteria for finding equilibrium phase compositions in complex systems by free-energy minimization is demonstrated. A criterion is proposed that is applicable to physicochemical systems of any complexity. The criterion in the general case amounts to solving an auxiliary problem, where any free-energy minimization algorithm can be used.

At present, investigation of equilibria in chemical systems by computation is being increasingly used in geochemistry and adjacent areas. However, the potential of physicochemical simulation provided by computing is far from completely utilized. Calculations on equilibria have been restricted to a comparatively narrow range of topics, due to the use of equilibrium criteria applicable only to relatively simple chemical systems. The present paper deals with an equilibrium criterion for a system of any complexity, which can include any number of phases of constant or variable compositions, including solid, liquid, and gaseous solutions of any numbers of the components.\*\*

The Gibbs phase rule restricts the maximum number of phases coexisting in equilibrium. However, as a rule it is not known in advance what phases form the equilibrium association, and therefore one usually incorporates all possible phases into the thermodynamic model for the chemical system (subsequently just called system), the number of these considerably exceeding the number defined by the phase rule. The problem in calculating the equilibrium composition therefore consists primarily in selecting the phase association (phase composition of the system) that gives equilibrium, and only then are the equilibrium compositions of these phases found. The solution to the second problem (that of calculating equilibrium in a system of given phase composition) is comparatively simple, and numerous algorithms and computer programs have been written for the purpose. However, no criterion has so far been defined that enables one to find the equilibrium phase association in the general case.

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\*\*Following [1], by components we understand qualitatively distinct parts of a single phase that are capable, at least in principle, of varying quantitatively independently one of another. For example, ions and neutral complexes are components of an aqueous solution, while any phase of constant composition contains only one component. Particular note should be made that the name independent components is given to stoichiometric units used to express the compositions of the dependent components.

In practice, various particular criteria are used for this purpose, which enable one to select a stable association only amongst phases of constant composition and in certain cases of ideal solutions.

The general scheme for identifying the equilibrium phase association is as follows. First one calculates the equilibrium for a given phase composition. Then one uses some suitable criterion to determine whether this solution is an equilibrium one for the system as a whole. If this is not so, the criterion should indicate what new phase association should be selected to bring the system closer to equilibrium. After suitable change in the phase composition, the calculation is repeated. The process terminates when the criterion indicates that the current phase composition provides equilibrium in the entire system.

For the isobaric-isothermal systems envisaged here, the equilibrium state corresponds to minimum free energy (Gibbs energy  $G$ ). This is the most general principle and is applicable to all systems at constant temperature and pressure, but it is not, strictly speaking, suitable for practical calculations. A direct check on the minimality of the free energy at a given point requires comparing this with the values of  $G$  for all other possible system compositions, which obviously is impossible. However, from the general concept of minimum free energy we can derive consequences that can be used to check the equilibrium state of a given composition. Of these, two are most used: the law of mass action and the Kuhn-Tacker condition.

The law of mass action is based on stoichiometric reaction equations; specification of such an equation for the computing system means that the corresponding reaction comes to equilibrium when the concentrations of the components of the phases involved in the reaction attain the values that satisfy the equation. The free-energy concept is not used explicitly in calculations of equilibria by means of the law of mass action, but minimization of  $G$  is understood inexplicitly, since the derivation of the equations is based on the requirement of a minimum in the total free-energy of the initial substances and reaction products. The law of mass action is a consequence of the condition of a minimum in the isobaric-isothermal potential, which can be used in computations on equilibrium conditions, but the law is only a particular case of the general criterion of  $\min G$ . An investigator who uses this equation must know in advance the reaction for which he writes the law of mass action and which will occur in the equilibrium. This condition is always obeyed for example for an ideal gas mixture. However, such equations cannot be written for reactions that go to completion, such as between phases of constant composition. The most complex problem that can be solved by this method is to calculate the equilibrium in a heterogeneous system consisting of a solution and several phases of constant composition related to the solution by solubility products.

The second criterion is the Kuhn-Tacker condition, and this occurs because of explicit formulation of the equilibrium calculation as minimization of  $G$ . The theory of mathematical programming is a division of computational mathematics that deals in part with the derivation of turning points in functions, and it gives us a criterion for checking the optimality of the composition, and also a set of methods of finding the optimum point. The Kuhn-Tacker theorem in one formulation asserts that a given point (system composition) is optimal (equilibrium) if the gradient in the target function  $G$  can be expressed as a definite linear combination of normals to the constraint surfaces (see [2] for all details on the Kuhn-Tacker conditions). The constraints in the present case are the equations (mass-balance equations) and inequalities (the conditions for the molar amounts of the components to be nonnegative,  $n \geq 0$ ). A very

important point is that the Kuhn-Tacker condition contains the chemical potentials of all components of the system no matter whether their amounts are non-zero or not. This enables one to use the approach in systems where reactions may go to completion. For example, the equilibrium composition can be determined for a system consisting only of solid phases that do not form solutions by minimizing  $G$  using the Kuhn-Tacker conditions as the equilibrium criterion (this is a problem in linear programming).

The Kuhn-Tacker conditions include the law of mass action as a particular case and therefore constitute a more general criterion. However, the equilibrium phase composition may be known in advance, in which case the two approaches are in principle equivalent. In that case, the use of the law of mass action even has a certain advantage, since in general the equilibrium constants for reactions can be derived more readily than the free energies for all components of the system.

The apparent universality of the Kuhn-Tacker conditions as criteria for equilibrium in a system is not however any basis for mechanical extension of the application to more complicated cases. There are constraints on the applicability of these conditions from a feature that plays a positive part in the above examples, namely the need to know the chemical potentials of components whose molar amounts in the current composition are zero. The question of the chemical potentials of these absent components requires more detailed discussion.

When a component of the system is a phase of constant composition, the chemical potential of this is constant, i.e., it does not vary when the molar amount of the component alters. The phase vanishes when the amount becomes zero, but the chemical potential remains the same up to the point where this phase vanishes. Conversely, if a phase of constant composition previously absent is formed again, the chemical potential is at once equal to the previous value. This feature enables one to use the Kuhn-Tacker conditions to specify the chemical potential of a phase of constant composition even when it is absent from the system. In other words, the vector for the gradient in  $G$  may be continuously defined up to the boundary of the region of definition corresponding to the condition  $n = 0$ , where  $n$  is the molar amount of the phase in the system.

In general, the Kuhn-Tacker conditions are applicable to each internal point in the set of permissible compositions, and also at those boundary points of this set at which the gradient in  $G$  can be continuously determined. However, this is not possible for all boundary points. A special point is constituted by a nodal point in the region of permissible compositions corresponding to the absence of a phase of variable composition for which the chemical potentials of the components are dependent on the phase composition.

As an example let us consider an ideal solution of a certain composition. The chemical potentials of the components in the solution are

$$\mu_j = \mu_j^0 + RT \ln x_j,$$

where  $\mu_j^0$  is the chemical potential of the pure component under the given conditions and  $x_j$  is the molar fraction of component  $j$  in the solution. Let the amount of solution diminish in such a way that the molar fractions of the components are unaltered. The vector for the chemical potentials of the components will clearly remain constant until the solution has completely vanished, and its limit will be equal to the initial vector. If we now alter the

relation between the amounts of the components in the initial solution and repeat the process, we get another limiting value for the chemical-potential vector. Therefore, the limit to the gradient of  $G$  as the amount of solution tends to zero will have infinitely many values dependent on the path by which the point was approached. This means that at this point the gradient in  $G$  cannot be determined in such a way as to be continuous.

The above argument has the following physical meaning. When a phase of constant composition is absent from the system, an infinitely small trial amount of this phase may be formed, whereupon one considers how the free energy of the system is altered. If  $\Delta G < 0$ , the occurrence of the phase reduces the free energy, and the phase should be formed; if  $\Delta G > 0$ , the new phase is unstable under these conditions (this is the meaning of the Kuhn-Tacker conditions that relate to absent phases). If on the other hand the solution phase is absent from the system, one cannot perform such a check, since the effect from formation of the "trial" solution may be substantially dependent on the composition of that solution. In that case the Kuhn-Tacker conditions are not applicable, and the state of equilibrium for the given composition must be determined from other and more general consequences by the condition for minimal potential.

Although it is explicitly assumed in the Kuhn-Tacker conditions that the partial derivatives of the target function exist, an attempt has been made [3] to apply these conditions to nodal points corresponding to absent solution phases. To discuss this result we follow Karpov in introducing the following symbol:

$$w_j = \mu_j^0 + RT \ln x_j - \sum_i a_{ij} u_i, \quad (1)$$

where  $a_{ij}$  are the stoichiometric coefficients for component  $j$  of the solution and  $u_i$  are the chemical potentials of the independent components (Lagrange multipliers). According to the Kuhn-Tacker theory, the condition  $w_j = 0$  is obeyed for all variables at the optimum point if the value of each such variable is positive, while  $w_j \geq 0$  if the variable is zero. Of course, the molar fractions  $x_j$  of the components of the solution have perfectly definite values if the solution exists, and (1) is meaningful. In that case the equation  $w_j = 0$  can be used and actually are used in certain algorithms for calculating equilibria in systems involving solutions. If on the other hand the solution is absent, the equilibrium conditions  $w_j \geq 0$  not only can be checked (because the  $x_j$  are not defined) but also in general have no meaning, because the necessary partial derivatives do not exist. If we transform the condition  $w_j \geq 0$  to the form

$$\exp \left[ \left( -\mu_j^0 + \sum_i a_{ij} u_i \right) / RT \right] - x_j \leq 0$$

and sum the resulting inequalities over all components of the solution following Karpov, who ignored the irregularity of these transformations, we obtained the condition

$$f_\alpha = \sum_i \exp \left[ \left( -\mu_j^0 + \sum_i a_{ij} u_i \right) / RT \right] - 1 \leq 0, \quad (2)$$

which is used in the selector program as an equilibrium criterion.

The derivation of the criterion still contains an obvious error: the Kuhn-Tacker theorem requires obedience to the condition  $w_j \geq 0$  for each variable, which is not guaranteed at all by the conditions  $f_\alpha \leq 0$ , since a

nonpositive value for the sum does not demonstrate that each term separately is nonpositive. It is shown below that nevertheless in one particular case the criterion  $f_{\alpha} \leq 0$  can be used.

#### EQUILIBRIUM CRITERION FOR A CHEMICAL SYSTEM

Instead of the free energy  $G$  let us consider for convenience the reduced energy  $g = G/RT$ , since these have their minima simultaneously (for given  $P$  and  $T$ ), and for brevity we will simply call this the energy. The standard energy of component  $j$  is denoted by  $g_j^0$ .

At some step in the minimization of  $g$  we will find an association of phases in equilibrium. We have to determine whether this association is stable.

Let us divide the vector  $n$  for the molar amounts of the components into two subvectors  $n_1$  and  $n_2$ . The components of the phases appearing in the initial association are represented by  $n_1$ ; the corresponding phases are called present. The phases whose molar amounts at a given step are zero are called absent; their components are represented by  $n_2$ .

A decision on the stability of the initial association is taken as follows. The initial association is stable if there is no reduction in  $g$  on the formation of any combination of phases of constant or variable composition whose components appear in  $n_2$ . Conversely, the association is unstable if there is a combination of phases (from components with  $n_2$ ) that reduces the energy.

The newly formed phases can arise only from the components in the present phases, so they cannot occur in arbitrary quantitative relationships, and the resulting solutions cannot have arbitrary compositions, i.e., some definite constraints are imposed in general on the compositions and amounts of the phases formed.

The independent components (stoichiometric units) used to express the compositions of the components may be selected arbitrarily to a considerable extent. For example, the composition of a mineral may be examined in terms of chemical elements, oxides, other minerals, or solution components. To derive an equilibrium criterion it is necessary to change to a new system of independent components by using as stoichiometric units those components from  $n_1$  that can be used to express the compositions of all the other components in  $n_1$ . Let the number of these basic components be  $r$ , and the number of independent mass-balance equations for the system be  $m$  ( $r \leq m$ ). After changing to the new independent components, the forms of the mass-balance equations are naturally altered, although the transformed system remains equivalent to the previous one, since the transformations involve only multiplying equations by numbers and adding equations. Let us consider the resulting transformed mass-balance equations. Because of the above choice of independent components, all components of the phase in  $n_1$  will be present in the first  $r$  equations and will not appear in the others. Therefore, the transformed system of material-balance equations can be divided into two subsystems:

$$H_1 n = b,$$

where matrix  $H_1$  contains the stoichiometric coefficients for the components of the present and absent phases and

$$H_2 n_2 = 0, \tag{3}$$

which contains only components of the absent phases ( $r - m$  equations). The right sides of the equations of (3) are zero, since the initial system satisfies all the mass-balance equations, including (3), while all the  $n_{2i} = 0$  for the current composition of the system. If new phases arise in the system, the composition (the vectors  $n_1$  and  $n_2$ ) can alter only in such a way that the mass-balance conditions remain met.

If infinitely small amounts of new phases are formed in a system, we can neglect the changes in the molar amounts and chemical potentials of the components of the present phases; this is equivalent to the phases arising in a system open with respect to the independent components of the present phases with constant chemical potentials  $\mu_r$ . It follows from [4] that the change to an open system can be performed by replacing the mass-balance equations by (3), and the thermodynamic potential of the system will be the Korzhinskiy potential  $g^K$ , which is defined by  $\nabla g^K = \nabla g - H'_1 \mu_r$ . One of the properties of the Korzhinskiy potential is that it is zero for all completely mobile components. In this system, new phases are formed from components of zero energy, and therefore the overall energy  $g^K$  is numerically equal to the energy effect from their formation. Then the condition for the stability of the initial association can be formulated as follows: a phase association is stable if  $g^K(n_2) \geq 0$  for any vector  $n_2$  that satisfies (3), i.e., the formation of any new phases or phase combinations cannot reduce the system energy.

The formation of phases in open system is related to the fact that once phases have arisen they can increase indefinitely. In fact, if  $n_2$  satisfies system (3), which should be obeyed for the phases formed, then the vector  $\alpha n_2$ , where  $\alpha$  is any positive number, should also satisfy this system. On the other hand, proportional change in the composition vector  $n_2$  will cause a proportional change in the system energy:

$$g^K(\alpha n_2) = \alpha g^K(n_2),$$

i.e., the sign of  $g^K$  will be the same at all points on a straight line arising from the origin (i.e., from the point  $n_2 = 0$ ). It is therefore sufficient to consider only one point on the straight line in each direction, which can be attained by introducing the additional constraint

$$\sum n_{2i} = 1. \quad (4)$$

This condition makes the region of possible values of  $n_2$  bounded, which enables one to formulate a constructive equilibrium criterion.

The criterion amounts to solution of the following problem in complex programming: find  $\min g^K(n_2)$  subject to the constraints of (3) and (4) and  $n_{2i} \geq 0$ . Let  $n_2^*$  be the solution to this problem, and then the initial phase association will be stable for  $g^K(n_2^*) \geq 0$  and unstable for  $g^K(n_2^*) < 0$ . In the latter case, the phases for which  $n_{2i}^* > 0$  should be included in the initial system and the minimization of  $g$  should be continued.

The criterion for minimality in  $g$  includes the problem of minimizing  $g^K$ , for which purpose one can use the minimality criterion again and so on. However, this process is finite, since the dimensions of the problem are reduced at each stage. It is therefore desirable to formulate this as a recursive procedure in writing a universal machine program for equilibrium calculation. The recursion halts when either there are no solutions amongst the absent phases or the constraints in the last problem consist of (4) alone. In the first case, the Kuhn-Tucker conditions are applicable, while we will examine the second in more detail.



The minimization of  $g^K$  with the single constraint of (4) may be interpreted as equilibrium calculation for an open system containing a single inert component. According to the phase rule for open systems [5], only one phase will be stable, which provides the minimum  $g^K$ . Therefore, the equilibrium composition of this system can be determined by considering each phase in sequence. The equilibrium value of  $g^K$  for the system will be at least of the phases thereby considered. The energy of phase  $i$  of constant composition is numerically equal to the standard energy  $g^K = g_i^{K0}$ , since from (4) we have  $n_i = 1$ . It is necessary to calculate the minimum possible energy for each phase of variable composition. This quantity can be found directly for an ideal solution. Let us write the Lagrange function for this problem:

$$\Phi = g^K + \lambda \left( \sum_i n_i - 1 \right) = \sum_i n_i (g_i^{K0} + \ln x_i) + \lambda \left( \sum_i n_i - 1 \right).$$

To determine the optimum point let us solve the system

$$\begin{cases} \partial\Phi/\partial\lambda = \sum n_i - 1 = 0, \\ \partial\Phi/\partial n_i = g_i^{K0} + \ln x_i + \lambda = 0. \end{cases} \quad (5)$$

We transform equations (5) to

$$x_i = \exp(-g_i^{K0}) \exp(-\lambda). \quad (6)$$

Summing these equations and substituting the resulting expression for  $\exp(-\lambda)$  into (6), we get the equilibrium concentrations of the solution components:

$$n_i = x_i = \exp(-g_i^{K0}) / \sum \exp(-g_i^{K0}). \quad (7)$$

If we have the concentrations of all components, we readily obtain an expression for the energy of the ideal solution:

$$g_{id}^K = -\ln \sum \exp(-g_i^{K0}). \quad (8)$$

This formula enables one to find the minimum energy of the ideal solution directly. If on the other hand the solution is not ideal, and the activity coefficients of the components are not given in advance, one can use an iterative procedure for minimizing the energy of this phase. In that case the component concentrations of (7) can be used as initial approximations. Note that (8) is applicable also to phases of constant composition if we formally consider such phases as one-component solutions: the substitution of the standard energy of the component into (8) gives  $g_{id}^K = g_i^{K0}$ .

On considering (2) and (8) we see that  $f_\alpha = \exp(-g_{id}^K) = 1$ , i.e., the condition  $f_\alpha \leq 0$  is equivalent to  $g_{id}^K \geq 0$ ; this makes clear the physical meaning of  $f_\alpha$ : it is determined by the minimum possible energy of an ideal solution on which no constraints are imposed. Therefore,  $f_\alpha$  cannot be used when real solutions may be formed. Further, even if all possible solutions are ideal, the  $f_\alpha$  criterion is not applicable if the initial phase association does not include all independent components (case  $r < m$ ). Therefore, let the initial association consist only of phases of constant composition, and it is required to determine whether the formation of an ideal aqueous solution reduces the energy. In that case, constraints must be imposed on the composition of the solution (these are not incorporated by the criterion  $f_\alpha \leq 0$ ); the number of these constraints is dependent on the number of phases from which the solution is formed, but in any case these will include the equation for electrical neutrality, since charge is not an independent component in the initial phase association.

## CONCLUSIONS

The calculation of equilibrium compositions for chemical systems has a specific feature that hinders the use of normal numerical methods of function minimization. The feature is that phases of variable composition may be formed, and traditional prediction methods are unsuitable for these.

Here a criterion is proposed that enables one to overcome this difficulty by reducing the calculation on the equilibrium in the system to that on equilibrium in the system to that on equilibrium in a simpler subsystem. The criterion is general in character, since it is applicable to systems of any complexity. The criterion is general because this derivation is not based on any specific properties of any class of solutions, and therefore the criterion is equally correct for ideal gas mixtures and for real solutions with restricted solubility and so on.

The criterion enables one to find the phase composition of the system at the equilibrium point, but it does not presuppose any definite method of finding the equilibrium amounts of the components of the given phases, thus leaving it possible to select algorithms that are the most effective for a particular class of system.

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