

# USE OF THE ELECTRICAL NEUTRALITY EQUATION IN CALCULATIONS ON THE EQUILIBRIUM COMPOSITIONS OF GEOCHEMICAL SYSTEMS\*

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It is shown that numerical methods of minimizing the free energy for geochemical systems containing water must incorporate the electrical-neutrality equation in the constraints. A method is given for incorporating this equation in calculating equilibrium compositions of minimization. Specifications are drawn up for algorithms and programs for universal use in hydrogeochemistry.

The methods of incorporating the electrical neutrality condition have an important effect on the reliability in simulating geochemical processes involving aqueous phases. There are two aspects. Firstly, the computation is made essentially more complicated by employing the electrical neutrality equation, because the schemes require linear independence for the conservation equations, which include the electrical neutrality one. However, in some cases the system is linearly dependent, which makes the calculation impossible and forces one to exclude the redundant equations for mass conservation (expressed in terms of the others). On the other hand, if the electrical neutrality equation is excluded without proper cause, the calculations are not hindered, but the result is certainly incorrect, since the aqueous solution appears electrically charged. Therefore, the algorithms and programs for calculating the equilibrium composition must at certain stages incorporate the choice of those conservation equations that provide a normal course for the calculations and an exact result. The second difficulty is related to the restricted number-representation range in computers. If the concentrations of certain components in the aqueous solution become so small that they can be represented in the computer only by pure zeros, then the corresponding terms in the conservation equations vanish, i.e., the forms of the equations are altered. As a result, the conservation equations may become linearly dependent, and an appropriate response to this must be envisaged in the algorithms.

## CHOOSING INDEPENDENT EQUATIONS

The electrical neutrality equation can be obtained as the sum of the conservation equations for the elements with coefficients equal to the valencies (charges) in a simple model for a system in which all the elements have unique valencies. In other words, the mass and charge conservation equations form a linearly dependent system, so one at least of these equations must be eliminated. One can eliminate any of the equations, and this is done in equilibrium calculations by substitution methods, with the electrical neutrality equation taken as one of the initial ones [1].

In the most general case, the model allows redox reactions, and then the neutrality equation cannot be expressed via the other conservation ones and must be incorporated to provide zero charge on the solution.

There are models for systems containing water that fall between these extreme cases, where the independence or otherwise of the neutrality equation is not so

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obvious; this topic is discussed in [2], where there is a study of the need for incorporating that equation in various models. The analysis was not carried through to an algorithmic realization, the purpose being to allow the researcher in each case to decide independently on the inclusion of that equation by examining the distributions of the variable-valency elements over the dependent components. On the other hand, it is quite simple to use linear-algebraic methods to determine the independence of that equation from the other constraints by means of an algorithm and software, which makes a preliminary examination of the physicochemical model unnecessary.

However, the basic disadvantage of that method is that the neutrality equation, which is necessary for describing a multisystem (i.e., when all possible phases are incorporated), may become redundant for certain phase compositions. We thus see that in general the necessity of the equation for a correct description cannot be solved in general form and must be solved afresh for each change in the phase assemblage. Further, this conclusion is more general, since it applies not merely to the neutrality equation. Let for example an anhydrous mineral system contain only those phases whose compositions can be expressed in terms of higher oxides. In that case, the conservation equations for oxygen and the other elements are linearly dependent, and so one of these equations must be deleted. However, the formation of any native element in that system (or of a mineral including an element in a more reduced state) makes it necessary to reintroduce the previously redundant conservation equation.

We therefore have that: a) the mass-conservation equations may be linearly dependent for certain phase compositions, and b) the algorithms should envisage checking for independence and eliminating surplus equations if necessary.

Methods of checking linear independence and distinguishing dependent equations are familiar. Gauss exclusion is the most convenient, but the choice of the equations to be excluded is not unique. If the calculations were performed with infinite accuracy, it would be sufficient to eliminate any of the equations expressed in terms of the others, and the arbitrary element in the choice would not affect the final result. However, numbers are represented in a computer with finite accuracy, so the result is in fact dependent on the exclusion algorithm to a substantial extent. The relative accuracy is the same for all the numbers represented in the computer (it is determined by the word length), so to provide the maximum accuracy in the equilibrium composition, one should eliminate those of the linearly dependent mass-conservation equations whose constant terms are largest in magnitude, i.e., contain the largest absolute errors. This means in particular that one should calculate for a homogeneous aqueous solution not containing ions of elements with variable valency while leaving the electrical neutrality equation in the system of constraints, and deleting the equation specifying the hydrogen conservation.

#### DEGENERATION IN THE MASS-CONSERVATION EQUATION

The linearly independent equation set is chosen from the stoichiometric coefficients for the dependent components, i.e., without allowance for the actual molar amounts. The current amounts (concentrations) are substituted into each conservation equation during the calculation, but these may be so small that they cannot be represented in the computer as positive numbers. Consequently, the corresponding terms vanish from the conservation equations, and consequently, the truncated equations may become linearly dependent. This degeneracy is solely a consequence of the constraints in computers and is not due to thermodynamic or algorithmic necessities.

It has been pointed out [2, 4] that the conservation equations may degenerate because all elements of variable valency go over virtually completely to the state of highest (or lowest) oxidation, and in [5] a detailed example was given of a case where this occurs. The recommendation was that the calculation should be simply repeated if the neutrality equation becomes practically redundant, with that equation deleted from the constraints, but this apparently natural solution is in fact erroneous.

The permissible set  $D$  of system compositions is specified by the constraints  $Hn=b$  and  $n \geq 0$ , while its dimensions are  $n - m$ , where  $n$  is the number of columns (variables) and  $m$  is the number of linearly independent rows (equations) in matrix  $H$ . If one deleted from  $H$  the row corresponding to the neutrality equation, one gets a change in the permissible set: the new set  $D_1$  has dimensions

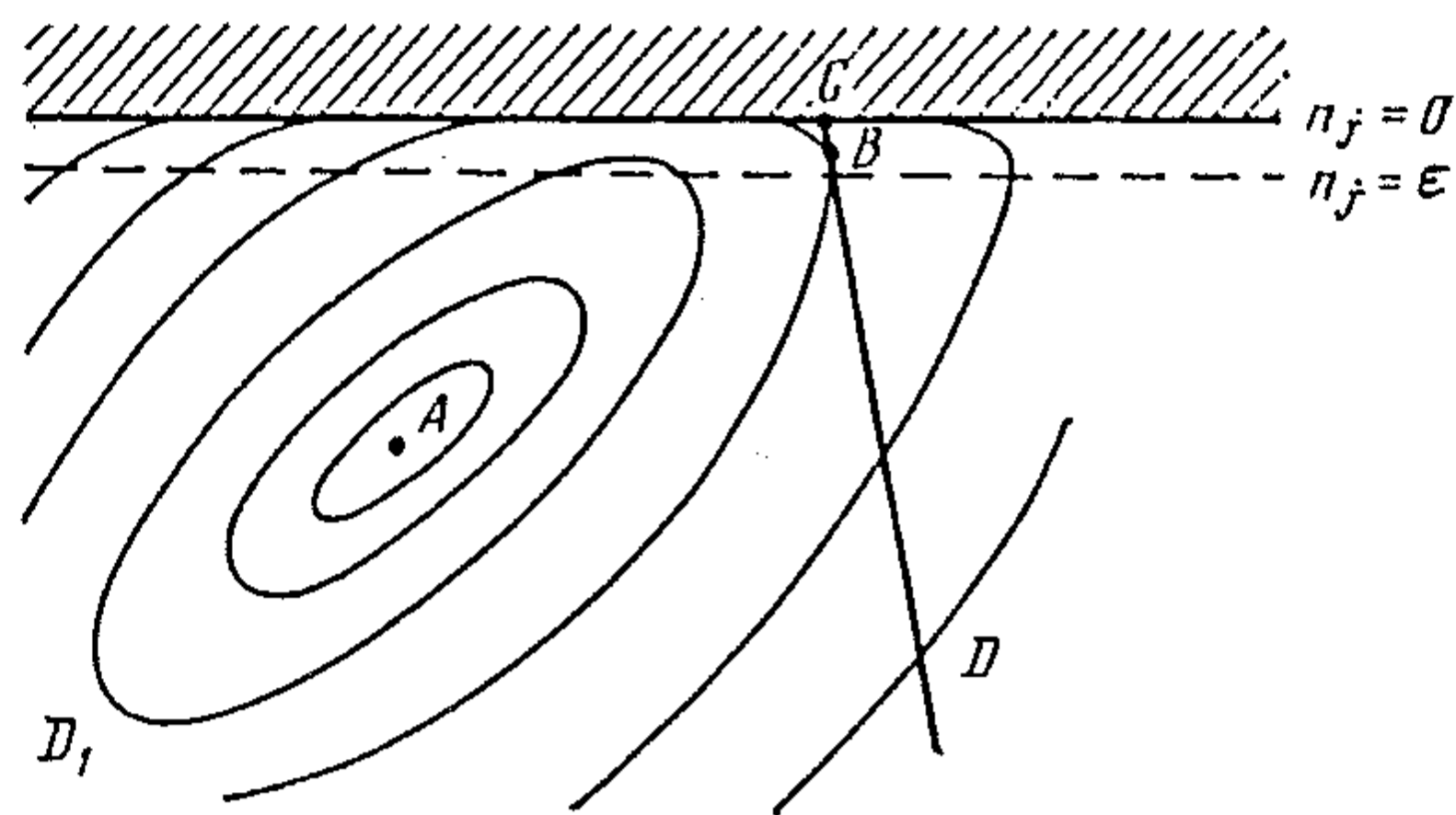


Fig. 1. Effects of the presence of the electrical neutrality equation on the calculated equilibrium composition (schematic); explanation in text.

$n - m + 1$  (i.e., is increased by one) and entirely includes the initial set  $D$ . As the permissible composition set is expanded considerably on eliminating the neutrality equation, one cannot expect that the solution to the new treatment, i.e., the point corresponding to minimum free energy in  $D_1$ , will fall in set  $D$ . In other words, if we exclude the neutrality equation, we will not obtain an electrically neutral solution.

This can be illustrated very readily. Figure 1 shows a two-dimensional permissible set  $D_1$  for a certain problem without the neutrality equation; it also shows the lines of equal potential. The minimum in the potential is attained at  $A$ . Now let the constraints be supplemented with the neutrality equation. This additional constraint reduces the dimensions of the permissible set by one, i.e., distinguishes in  $D_1$  a subset  $D$  (here a straight line) for the electrically neutral compositions;  $D_1$  is split into two parts: regions with positively and negatively charged compositions. The free-energy minimum in  $D$  is attained at  $B$ , and this point is the true solution. We assume that  $B$  lies so close to the boundary of the permissible composition set that the concentrations of the corresponding solution components at that point cannot be represented by positive numbers in the computer (the boundary is defined by the condition  $n_j = 0$  and theoretically is never attained). Then during the treatment (i.e., as  $B$  is approached), a point is reached where the constraint system degenerates, i.e., the mass and charge conservation equations become linearly dependent. If in that situation one excludes the redundant neutrality equation, the region of permissible compositions becomes  $D_1$ , and one obtains composition  $A$  as the solution. It is clear that this apparent solution is not satisfactory.

The escape lies not in excluding the neutrality equation (which should always be present in the constraints) but in deleting those dependent components from the stoichiometric matrix whose molar amounts have become so small as to lead to the equations degenerating. Of course, deleting some of the dependent components alters the constraints, which in turn requires redetermination of the linearly independent subsystem of equations as above. In that case, the solution will be composition  $C$ , which coincides within the machine accuracy with  $B$ .

A feature of this solution is that one cannot obtain the equilibrium redox potential from it (although one can state the interval in which  $E_h$  lies). On the other hand; as the degeneracy is due only to technical features of the computer, the equilibrium  $E_h$  cannot be calculated at all for that system with that machine without using some additional information.

In practice, degeneracy in the constraint system is fairly rare, occurring in highly reducing or oxidizing circumstances, so  $E_h$  is usually readily calculated. It is therefore possible that researchers employing computer simulation often overestimate the accuracy in the  $E_h$  obtained in this way. In a closed system,  $E_h$  is always very sensitive to errors in the overall composition, particularly for oxygen and hydrogen, whose molar amounts in water-bearing systems often exceed those of elements of variable valency by many orders of magnitude. Sometimes, the absolute error in representing the amounts of  $H_2$  and  $O_2$  are actually

larger than the amount of a component that may be oxidized, in which case the calculated Eh is absolutely unreliable. Although the neutrality equation enables one to improve the accuracy somewhat for redox reactions, a separate discussion is needed to obtain a radical solution for generating accurate Eh.

## COMPATIBILITY IN THE MASS CONSERVATION EQUATIONS

The following is a further argument for the essential inclusion of the neutrality equation in the system. If the constraint system is to describe the permissible composition set, it must be compatible, since it consists of the conservation equations and the conditions for nonnegativity of the molar amounts of the dependent components. For example, if the stoichiometry of the charge conservation equation means that it can be represented as a linear combination of the mass conservation equations, then the same combination of the constant terms gives the overall charge. If the overall charge calculated in this way is zero, this means that the system of conservation equations is linearly dependent, i.e., it is necessary to select an independent subsystem. If on the other hand the overall charge differs from zero, the constraint system is incompatible, i.e., the set of permissible compositions is empty, and the problem has no solution. This example shows the significance of the overall composition for constraint compatibility.

In most algorithms, it is assumed that the constraints are compatible, but this is not confirmed by an appropriate algorithm or program. Therefore, the stoichiometrically dependent neutrality equation is eliminated by the user from the constraint system manually, i.e., at the stage of preparing the job. As a result, possible errors in specifying the overall composition are not detected. For example, the composition of sea water used by many researchers as a check example [1, 6, 7] contains a considerable charge unbalance. However, even if the solution contains ions of variable valency and the neutrality equation is included in the constraints, this does not guarantee that the constraint system is compatible in all cases. For example, the overall composition of the multi-system consisting of an aqueous solution with solid phases given in [4] as a test problem has a considerable positive charge, which cannot be compensated even if all the Fe present in the system (the only element of variable valency) is converted to the divalent state. In that case, the degeneracy in the constraints (which led the authors to eliminate the neutrality equation) occurred only because the permissible composition set was empty, but this was not detected. These examples show that checking the compatibility in the constraint system (essentially including the neutrality equation) is a necessary element in the algorithm.

## CONCLUSIONS

Reliability in simulating the equilibrium state in a system containing water is dependent to a considerable extent on the methods used to incorporate the electrical neutrality condition. Algorithms and programs for calculating equilibrium compositions for general application in hydrogeochemistry should meet the following requirements.

1. The algorithm should necessarily include the electrical neutrality equation amongst the constraints.
2. Before calculations are made, a check should be made on the constraint compatibility, i.e., that the provisional composition set is not empty.
3. With every change in phase composition or dependent-component set, a fresh check should be made on the linear independence of the constraints, and if necessary, an independent subsystem of conservation equations should be selected to provide the maximum accuracy.
4. If the iteration degenerates because all the oxidized or reduced forms vanish, the calculations should be continued after the vanishing dependent components have been deleted from the stoichiometric matrix.

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## DETERMINING RADON MIGRATION TIMES IN AQUIFER-BOREHOLE SYSTEMS FROM DECAY-PRODUCT ACCUMULATION\*

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That radon can be used as a geochemical precursor for earthquakes was first demonstrated [1-3] by studies of variations in its concentration in groundwater occurring before the Tashkent earthquake of 1966 and after it. Subsequent research on radioactive and radiogenic elements as earthquake precursors has shown that the individual representatives of these groups differ in informativeness, and different sources (springs and boreholes) are also not equivalent [4-8]. It has been considered [5-8] that boreholes in fault zones are the most informative, but this is an inadequate criterion, since boreholes located quite close together often give different effects in the periods preceding earthquakes [6-8]. It is also not confirmed that depth is decisive in the informativeness of a borehole [6]. In this connection, it remains important to evaluate the informativeness of boreholes and other water sources in seismic forecasting.

Recently, arguments have been advanced that borehole informativeness here is dependent on the hydrodynamic features, particularly the time spent by the components in the system, the damping coefficients, and so on [6, 9-12]. The approach appears very promising, although there are certain difficulties in calculating or otherwise determining the necessary parameters. Here we will consider radon in relation to the informativeness of observation points, particularly the duration of the migration in the aquifer-borehole system.

If one considers the occurrence of a hydrogeochemical precursor as a burst of tracer content in groundwater due to change in the state of strain in the

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