Equilibrium solution methods for ionospheric reaction systems

HAROLD CITRYNELL

International Meteorological Institute,
University of Stockholm, Sweden

ABSTRACT. An iterative method is derived for obtaining an equilibrium solution for ionospheric reaction systems involving positive ions and electrons. Another method for obtaining the same equilibrium solution is also given and, in addition, a method is described for obtaining an equilibrium solution for ionospheric reaction systems involving negative ions, positive ions and electrons.

1. Introduction

The analysis of chemical reactions involving ionization may be frequently reduced to a set of reaction rate equations and if it is known that the system has reached a state such that the concentration of any constituent involved undergoes negligible changes with time, the analysis may be further simplified by using a set of equilibrium equations which are formed by setting the rate equations equal to zero. Sometimes, as in the case of atmospheric ionic reactions, a system of non-linear algebraic equations result that must be solved by numerical methods. In some cases, even if a good set of initial values are selected, the system will diverge unless special methods are used to make the system converge to their final values. A method that will force the system to converge is derived here.

2. Derivation

Consider a system of n equations having the form

$$x_j = \left(a_j + \sum_{\substack{k=1 \\ k \neq j}}^{n} a_{jk}.x_k \right) \Big/ \left(b_j + y \right),$$
$$(j = 1, 2, \ldots n) \quad (2.1)$$

in which

$$y = \sum_{j=1}^{n} x_j \qquad (2.2)$$

and x, a, and b are positive quantities. Eq. (2.1) corresponds to the equilibrium equations of the chemical reaction system and Eq. (2.2) corresponds

to the condition that the electron concentration equals the sum of the concentrations of the positive ions (for the case where the negative ions may be neglected as, for example, the atmospheric ionic reaction system above 80 km). If the left-hand member of Eq. (2.1) is multiplied by $(b_j + y)$ and if n of these are summed, the result is

$$\sum_{j=1}^{n} b_j.x_j + y. \sum_{j=1}^{n} x_j = \sum_{j=1}^{n} \left(a_j + \sum_{\substack{k=1 \\ k \neq j}}^{n} a_{jk}.x_k \right) \quad (2.3)$$

During any stage of iterative calculations, it is possible to find a value, $\bar{b}$, such that

$$\bar{b} = \left(\sum_{j=1}^{n} b_j.x_j \right) \Big/ \left(\sum_{j=1}^{n} x_j \right) \qquad (2.4)$$

Using the symbol, R, to represent the right-hand member of Eq. (2.3), and by using Eq. (2.2), Eq. (2·3) may be rearranged to be

$$y^2 + \bar{b}.y - R = 0 \qquad (2.5)$$

Solving Eq. (2.5) for y yields

$$y = [-\bar{b} + (\bar{b}^2 + 4.R)^{1/2}]/2 \qquad (2·6)$$

Hence, each iteration cycle requires the calculation of $\bar{b}$ by Eq. (2.4), y by Eq. (2.6), and x_j in Eq. (2.1). An assumed value for y may be used to start the iteration.

TABLE 1

Convergence of the system

Iteration		0	1	2	3	Solution
x_1	(10^3)	1·493	1·554	1·521	1·544	1·536
x_2	(10^2)	4·79	7·32	5·71	6·74	6·33
x_3	(10^3)	2·77	9·11	4·11	6·66	5·46
x_4	(10^4)	3·50	18·41	5·92	11·59	8·72
x_5	(10^3)	1·537	1·728	1·607	1·682	1·652
sum	(10^4)	4·13	19·72	6·70	12·64	9.65
$\bar{b}$	(10^5)	4·42	1·025	2·84	1·562	2·01
R	(10^{10})	2·65	3·08	2·78	2·95	2·88
y	(10^4)	20·0	5·35	13·15	7·71	9·65

3. Calculations

A set of gaseous reaction rate equations which occur in the lower E region of the ionosphere, during an electron precipitation event, were solved for the ionic concentrations of N_2^+, N^+, O^+, O_2^+ and NO^+ using the method described in the preceding section. The set of equilibrium equations for these rate equations, which correspond to Eqs. (2.1) and (2.2), are

$$x_1 = \frac{5.60 \times 10^9}{3.55 \times 10^6 + y} \tag{3.1}$$

$$x_2 = \frac{2.03 \times 10^8}{2.24 \times 10^5 + y} \tag{3.2}$$

$$x_3 = \frac{5.35 \times 10^8 + 3.31 \times 10^4 \, x_1}{1.088 \times 10^4 + y} \tag{3.3}$$

$$x_4 = \frac{1}{y}\left[3.28 \times 10^9 + 6.50 \times 10^5 x_1 + 4·15 \times 10^6.x_2 + 2.77 \times 10^5.x_3 \right] \tag{3.4}$$

$$x_5 = (8.06 \times 10^6 x_1 + 1.960 \times 10^6 x_2 + 5.95 \times 10^4.x_3 + 1.095 \times 10^2.x_4)/(8.35 \times 10^6 + y) \tag{3.5}$$

$$y = \sum_{j=1}^{5} x_j \tag{3.6}$$

Table 1 shows the convergence of this system of equilibrium equations to a solution by means of the derived method. The solution gives the concentrations in units of ions/cm³ (corresponding to the above mentioned atmospheric ions, in the same order). The electron concentration equals the sum of the positive ions for this problem.

4. Discussion

There is another method of forcing the system of Eqs. (2.1) and (2.2), to converge to the solution values which has been used successfully by the author for similiar problems. Given an ionospheric reaction system, not involving negative ions, [e.g., Eqs. (2.1) and (2.2)], the total ion concentration, Σx_j, decreases as the selected electron concentration, y, increases. By the condition that the electron concentration equals the sum of the concentrations of the positive ions, $y_{sol} = \Sigma x_j$, represents that value of y which satisfies Eqs. (2.1) and (2.2). Hence, if the value selected for y is smaller than y_{sol}, then $\Sigma x_j > y_{sol}$, and if $y > y_{sol}$, then $\Sigma x_j < y_{sol}$. Therefore if y_i is a value for y at step i, which yields $(\Sigma x_j)_i$, a better value for y for the next step will be

$$y_{i+1} = \left[y_i + \left(\sum_{j=1}^{n} x_j \right)_i \right] / 2 \tag{4.1}$$

This simple technique will also force the system to converge to a solution for a reasonably realistic intital estimate of the electron concentration, y_0.

The principle used for the solution of a system of ionospheric equations that do not include negative ions, given by Eq. (4.1), may be extended to include the region of the atmosphere below about 80 km in which negative ions, as well as positive ions, are important to take into account. For this

case, the equilibrium ionospheric reaction system may be represented by $m+n$ equations,

$$x_j = \left[a_j + \sum_{\substack{k=1 \\ k \neq j}}^{n} a_{jk}.x_k \right] \Big/ \left[b_j + \sum_{k=1}^{m} b_{jk}.z_k + \right.$$

$$\left. +y \right], \quad (j = 1, 2, \ldots, n) \qquad (4.2)$$

$$z_p = \left[c_p.y + \sum_{\substack{k=1 \\ k \neq p}}^{m} c_{pk}.z_k \right] \Big/ \left[d_p + \sum_{k=1}^{n} d_{pk}.x_k \right],$$

$$(p = 1, 2, \ldots, m) \qquad (4.3)$$

in which

$$\sum_{j=1}^{n} x_j = \sum_{p=1}^{m} z_p + y \qquad (4.4)$$

where,

x_j, z_p, y represent positive ion, negative ion and the electron concentration respectively. Since electron attachment is the initial process in the formation of negative ions, the sum of the concentrations of negative ions may be written as

$$\sum_{p=1}^{m} z_p = \lambda.y \qquad (4.5)$$

where λ is a parameter whose value depends upon the entire reaction system.

In view of Eq. (4.4), the sum of the positive ion concentrations would be

$$\sum_{j=1}^{n} x_j = (1 + \lambda).y \qquad (4.6)$$

The iteration process, for the region, including negative ions, may be begun by using the following initial values: the sum of the negative ion concentrations is assumed to be zero, $\lambda_0 = 0$ and the sum of the positive ion concentrations is taken as being equal to the assumed electron concentration. Next, the concentrations of the individual nega-

tive ions are calculated and summed, so that for an iteration step, i, the value for λ_i is given by

$$\lambda_i = \left(\sum_{p=1}^{m} z_p \right)_i \Big/ y_{i-1} \qquad (4.7)$$

The concentrations of the individual positive ions are then calculated and summed. This value decreases when the electron concentration increases. If the sum of the positive ion concentrations were calculated by Eq. (4.6) the value of this sum increases when the electron concentration increases. Hence, at a given electron concentration, the average of these two values will be closer to the intersection of the curves representing these two functions than either value,

$$\left(\sum_{j=1}^{n} x_j \right)_{i,\text{av}} = \left[\left(\sum_{j=1}^{n} x_j \right)_i + \right.$$

$$\left. +(1 + \lambda_i) \, y_{i-1} \right] \Big/ 2 \qquad (4.8)$$

and by means of Eq. (4.6), the electron concentration corresponding to this average value, for iteration step i, is

$$y_i = \left[\left(\sum_{j=1}^{n} x_j \right)_i + (1 + \lambda_i).y_{i-1} \right] \Big/ \left[2.(1 + \lambda_i) \right] \qquad (4.9)$$

An iteration cycle includes calculating the sum of the negative ion concentrations, λ_i by means of Eq. (4.7), the sum of the positive ion concentrations, and the electron concentration by means of Eq. (4.9). The iteration, process is repeated until the electron concentration approaches a constant value, within a given limit of accuracy, and the condition of charge neutrality, Eq. (4.4), holds within allowable limits. Thus it is seen that Eq. (4.8) is similar in concept to Eq. (4.1), which was used for the solution of a system of ionospheric equations that does not include negative ions.

It should be noted that the same principles apply even if the reaction system includes three body reactions.