

NOTE ON THE CALCULATION OF A COMPLEX CHEMICAL EQUILIBRIUM IN IDEAL GASEOUS SYSTEMS

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The paper is devoted to some aspects of numerical solution of the problem of chemical equilibrium in ideal gaseous mixtures.

In the paper¹ a method was published for calculating the complex chemical equilibrium in ideal gaseous systems. The calculation is based on the determination of the minimum of the total free enthalpy of the system by the method of coupled extremes (Lagrange multipliers). To solve the resulted system of equations (9) in the work cited¹, a combination of the gradient and the Newton methods was used. This procedure was chosen in order that the advantages of both methods (the certainty of the convergence of solution of the gradient method and a low number of steps needed with the Newton method) might be employed. A similar procedure had been proposed already before that, e.g. by Marquardt². It was found that the method proposed can be substantially simplified by solving the system (9) directly by the generalized Newton method. The principle of this method is expressed by the relation (29) of the work¹. In order that such a method may be used universally it is necessary to prove the possibility to reach the convergence of the solution. An important property of the system (9) with respect to the convergence of the generalized Newton method is the fact that the functions on the left hand side of the system (9) are monotone and convex in all variables (and in the unknown quantity t even linear). To warrant the simplicity of the record and the lucidity of the proof, the discussion of the convergence will be carried out for one nonlinear equation and one unknown variable. To this purpose let us consider the function

$$f(x) = 0. \quad (1)$$

Let $f(x)$ be a continuous monotone (without loss of generality, we will assume an increasing) and convex function in the interval $\langle a, b \rangle$, where there is the only root of Eq. (1), too, which let be denoted by \bar{x} . If $x_n \in \langle a, b \rangle$ is the n th approximation of the root x , then it holds³

$$x_{n+1} = x_n - \varepsilon [f(x_n)/f'(x_n)]. \quad (2)$$

Now let us choose an arbitrary $x_0 \in \langle a, b \rangle$. Two cases can just occur:

$$x_0 \in \langle \bar{x}, b \rangle. \quad (a)$$

Then it holds³ $\bar{x} < x_n < x_{n-1} \dots < x_1 < x_0$,

$$\lim_{n \rightarrow \infty} x_n = \bar{x}, \quad (3)$$

if we set $\varepsilon = 1$ in the relation (2). It is evident that for this case even the classic Newton method converges.

$$x_0 \in \langle a, \bar{x} \rangle. \quad (b)$$

In this case the value of x_1 calculated from the relation (2) for $\varepsilon = 1$ falls either into the interval $\langle \bar{x}, b \rangle$ and then the case stated as (a) occurs or $x_1 > b$. If $x_1 > b$ then by halving the value ε we obtain $\bar{x}_1 \in \langle a, b \rangle$ for which $\bar{x}_1 > x_0$ holds. If $\bar{x}_1 \in \langle \bar{x}, b \rangle$ then, as well the case marked as (a) occurs or $\bar{x}_1 \in \langle x_0, \bar{x} \rangle$. Thus, a better approximation of the value \bar{x} than the value x_0 is obtained.

By repeating this algorithm, we obtain a sequence of x_i ($i = 1, 2, \dots$) which obviously converges to the solution of Eq. (1). Since it is possible to carry out this verification for any equation of the system (9) of the paper¹, it is to be considered proved that the application of the generalized Newton method to the above-mentioned system gives the convergent solution. By using the generalized Newton method for the solution of complex chemical equilibria in ideal gaseous systems, the substantial abridgement of the calculation can be reached. The time required for the calculation, compared with the method proposed in the paper¹, is reduced on the average more than four times.

REFERENCES

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