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ACCELERATION OF THE AFFINE SCALING METHOD CONVERGENCE FOR OPTIMISATION PROBLEMS OF THERMODYNAMICS

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The affine scaling method is used to solve two classical extremal problems of thermodynamics. The effective techniques for convergense acceleration are devised and realesed and the examples are presented.

Key words: affine scaling method, dual variables, free Gibbs energy function, entropy, acceleration of convergence.

1 Introduction

The paper presents and studies algorithms of searching for optimal and feasible solutions. Consideration is given to classical extremal problems of thermodynamics: minimization of the free Gibbs energy function and maximization of entropy. These interesting problems can be solved by the suggested algorithms of the affine scaling method [Dikin, 1998]. Here the vector of dual variables, that have an informal interpretation in both problems under investigation, is assigned to each interior feasible point.

The authors have revealed fast convergence of a sequence of dual variables to the dual problem solution [Dikin and Popova, 1997]. This experimental fact forms the base for devising and realization of effective ways to speed up convergence at determination of the thermodynamic equilibrium at constant pressure (p) and temperature (T), as well as, at study of the entropy model (in this case p and the enthalpy $H(x,T)$ are fixed, where x is the vector of substance content).

The suggested simple formulas to improve an approximate solution allow the feasible solution and dual variables satisfying optimality conditions within a high range of accuracy to be obtained in a small number of iterations. The affine scaling method efficiency is demonstrated on the examples.

Note that the algorithm for improving a feasible solution is a variant of the projective gradient method. A variant of the Newton method is applied for determination of an interior feasible point [Dikin, 1999]. At the investigation of optimization problems the process of obtaining a higher value of the objective function alternates with search for the interior feasible point, when there are nonlinear equations among the constraints.

2 Minimization of the free Gibbs energy function

2.1 Problem statement

Equilibrium of a system of reacting substances is achieved at the minimum of corresponding thermodynamic potential. Equations of the substance conservation have the form:

$$\sum_{j=1}^{n} a_{ij} x_j = b_i, \qquad i = 1, \ldots, m; \tag{1}$$

$$x_j \geq 0, \qquad j = 1, \ldots, n, \tag{2}$$

where a_{ij} — the number of atoms of species i in the j-th chemical compound; b_i — the total amount of moles with i-th chemical element of the system; x_j — the value of moles in compound j; $b = Ay$, y — the vector of initial reagents.

It is obvious that $a_{ij} \geq 0$, in this case there is at least one positive element in each column of the matrix $\|a_{ij}\|$. Therefore, the polyhedral convex set (1), (2) is bounded; such a set is referred to the polytope.

If the process proceeds at the constant temperature (T) and constant pressure (p), the function of the free Gibbs energy is minimized

$$G(x) = \sum_{j=1}^{n_1} \Big[G_j^0(T) + RT \ln\Big(p x_j / \sigma(x) \Big) \Big] x_j + \sum_{j=n_1+1}^{n} G_j^0(T) x_j \tag{3}$$

on polyhedron (1), (2), where G_j^0 — the standard mole Gibbs energy of substance j; R — the universal gaseous constant; n_1 — the number of substances in the gaseous phase, other substances, if available, belong to the condensed phase; $\sigma(x) = \sum_{j=1}^{n_1} x_j$ — the number of moles of substances in the gaseous phase.

The list of compounds, y, T, p are initial data for this problem. First input data then construct the matrix A, determine coordinates of the vector b and calculate $G_j^0(T)$ with the use of the database.

2.2 Optimality conditions

It is known that the extremum problem (3), (1), (2) is a convex programming problem. Let the minimum of objective function (3) at constraint

(1), (2) be achieved in the point x', then

$$\sum_{i=1}^{m} a_{ij} u'_i = \frac{\partial G(x')}{\partial x_j}, \quad x'_j > 0; \tag{4}$$

$$\sum_{i=1}^{m} a_{ij} u'_i \le \frac{\partial G(x')}{\partial x_j}, \quad x'_j = 0; \tag{5}$$

here $u' = (u'_1, \ldots, u'_m)$ is the vector of Lagrangian multipliers.

Moreover, from [Kaganovich, Filippov, Antsiferov, 1989, Zeldovich, 1938] follows that $x'_j > 0, \quad j = 1, \ldots, n_1$. Therefore, inequalities in (5) may take place only for components of the condensed phase.

George B. Dantzig proposed generalization of the simplex method for solving problem (3), (1), (2) [Dantzig, 1963].

Now we will describe the process for improvement of the feasible vector that belongs to the interior of the polyhedron (1), (2).

2.3 Iterative algorithm

Let the vector $x^0 > 0$, be given, moreover $Ax^0 = b$.

For the sake of reader's convenience the method of determining an interior feasible point x^0 is given bellow.

Determine dual variables $u_1^k, \ldots, u_m^k$ at the k-th iteration before computing the coordinates of vector x^{k+1}. For this purpose, with the known x^k, find the minimum of the function

$$\sum_{j=1}^{n} \left[x_j^k \Big(\sum_{i=1}^{m} a_{ij} u_i - \frac{\partial G(x^k)}{\partial x_j} \Big) \right]^2. \tag{6}$$

Now we have

$$x_j^{k+1} = x_j^k (1 + \lambda_k x_j^k \delta_j^k), \;\; \delta_j^k = \sum_{i=1}^{m} a_{ij} u_i^k - \frac{\partial G(x^k)}{\partial x_j}, \quad j = 1, \ldots, n. \tag{7}$$

The step λ_k is applied such that $x^{k+1} > 0$. Determine

$$\lambda'_k = \rho / \varphi_k, \qquad 0.5 \le \rho < 1, \tag{8}$$

$$\varphi_k = \max_{1 \le j \le n} (-x_j^k \delta_j^k), \;\; \lambda_k = \min(\lambda'_k, \;\; \lambda''_k). \tag{9}$$

The vector $x^k + (1/\varphi_k) s^k$ belongs to a boundary of polytope (1), (2), $G(\tilde{x}^{k+1}) < G(x^k)$, where $\tilde{x}_j^{k+1} = x_j^k + \lambda''_k s_j^k$, $s_j^k = (x_j^k)^2 \delta_j^k$, $j = 1, \ldots, n$.

Therefore, $G(x^{k+1}) < G(x^k)$, that is the objective function strictly decreases.

Let $\Phi_k = \sum_{j=1}^{n}(x_j^k \delta_j^k)^2$, if

$$\sqrt{\Phi_k} < \epsilon \quad \varphi_k < \epsilon_*, \tag{10}$$

then calculations terminate.

2.4 Acceleration of the algorithm convergence

Application of algorithm (6) – (10) results in rapid convergence of the sequence of dual variables $\{u^k\}$. In a small number of iterations, for example at the l-th one, we obtain a point u^l, which insignificantly differs from the vector u', that is a solution of the dual problem. Some coordinates of the vector x' can be small at $j \in J_*$. Hence, it is difficult to achieve satisfactory approximation of the numbers x'_j $(j \in J_*)$ using algorithm (6) – (10).

It should also be noted that the use of our method leads to large and negative discrepancies

$$\delta_j^l = \sum_{i=1}^{m} a_{ij} u_i^l - g_j^l, \qquad j \in J_*.$$

If x^l, u^l are optimal solutions of primal and dual problems, respectively, then according to (4) δ_j^l is bound to be equal to zero at $j \in J_*$.

For determining the numbers x_j^* let us consider the equations:

$$\sum_{i=1}^{m} a_{ij} u_i^l = G_j^0(T) + RT \ln\Big[p x_j / \sigma(x^l)\Big], \qquad j \in J_*. \tag{11}$$

Here x_j are unknown variables, therefore

$$x_j^* = \frac{\sigma(x^l)}{p} \exp(\bar{\delta}_j^l),\ \bar{\delta}_j^l = \Big(\sum_{i=1}^{m} a_{ij} u_i^l - G_j^0(T)\Big) \Big/ (RT), \quad j \in J_*$$

is the solution in (11).

Values of x_j^* are good approximation for numbers x'_j at $j \in J_*$. Note that

$$x_j^* = x_j^l \exp[\delta_j^l \,/\, (RT)]. \tag{12}$$

Refinement of the approximation solution. Using formula (12) we obtain x_j^* for all components of the gaseous phase ($j \leq n_1$) after determining the pair $(x^l,\ u^l)$. For condensed substances assume that

$$x_j^* = 0, \quad \delta_j^l < \bar{f} < 0, \ j > n_1, \tag{13}$$

where $\bar{f}$ is a negative number and, as a rule, is sufficiently large in the absolute value.

Usually equations (1) of the material balance are not satisfied in the point $x^* = (x_1^*, \ldots, x_n^*)$. Therefore, let us apply the algorithm for determination of the interior feasible point x^{l+1} with starting point x^*.

Accuracy of the fulfilment of optimality conditions (4) is higher for $(x^{l+1},\ u^{l+1})$ than in the point $(x^l,\ u^l)$. This refinement procedure can be used more than once.

2.5 Examples

The examples are presented only for illustration of the algorithm convergence.

Burning of carbon in oxygen.

Table 1
$T = 300$ K; $p = 1$ atm

Components	y	x^0	x^7	δ^7	x^*	x^8
C	1.0	1.0	$4.16 \cdot 10^{-4}$	$-8.3 \cdot 10^5$	$4.5 \cdot 10^{-148}$	$4.5 \cdot 10^{-148}$
CO	0.0	0.125	$2.02 \cdot 10^{-3}$	$-1.3 \cdot 10^5$	$2.1 \cdot 10^{-26}$	$2.1 \cdot 10^{-26}$
CO_2	0.0	0.125	0.99756	0.6854	0.99784	1.0000
O_2	1.0	1.0	$1.43 \cdot 10^{-3}$	$-2.0 \cdot 10^5$	$7.0 \cdot 10^{-39}$	$7.0 \cdot 10^{-39}$

Using formula (12) refinement begins after iteration 7 at $T = 300$ K (Table 1). Here $l = 7,\ J_* = \{1, 2, 4\},\ G(x^7) = -456719.454488, G(x^*) = -456619.9115,\ G(x^8) = -457609.47556$.

All components in the equilirium compound are positive, that is bound to be. At the same time the concentration of carbon is negligibly small. The matrix B^8 is ill-conditioned, therefore calculations terminate after obtaining the feasible point x^8. The vector x^k is assumed to be feasible, when $\|r^k\| < \epsilon_1,\ r^k = b - Ax^k,\ \epsilon_1 = 10^{-10}$.

If $(x_j^k)^2$ in (6) is substituted by x_j^k, then we obtain $x^* = (3.4 \cdot 10^{-156},\ 1.8283 \cdot 10^{-30},\ 1.0000,\ 9.1416 \cdot 10^{-31})$ with the help of (12). Such choice of the weighting coefficients is applied in [Detkovskaya, Chudnenko, Karpov, 1988]. In the authors' opionion it is possible to use at first the base variant of the method and then to consider the numbers x_j^k as weighting coefficients to terminate calculations. A similar technique for accelerating convergence is recommended in [Dikin and Zorkaltsev, 1980].

At same y l also equal to 7 at $T = 1500$ K (Table 2). Here the refinement procedure get 4 time, on iterations with even numbers is $\|r^k\| > \epsilon_1,\ \epsilon_1 = 10^{-10}$.

T a b l e 2
$T = 1500$ K; $p = 1$ atm

Components	x^7	x^9	x^{11}	x^{13}	x^{15}
C	$5.72 \cdot 10^{-4}$	$5.6 \cdot 10^{-27}$	$8.1 \cdot 10^{-28}$	$1.40 \cdot 10^{-27}$	$1.50 \cdot 10^{-27}$
CO	$7.04 \cdot 10^{-4}$	$1.1 \cdot 10^{-4}$	$3.2 \cdot 10^{-4}$	$3.66 \cdot 10^{-4}$	$3.61 \cdot 10^{-4}$
CO_2	0.99239	0.99989	0.99968	0.99863	0.99964
O_2	$4.09 \cdot 10^{-3}$	$5.3 \cdot 10^{-5}$	$1.6 \cdot 10^{-4}$	$1.83 \cdot 10^{-4}$	$1.81 \cdot 10^{-4}$

Table 3 illustrates change in the values which are impotant for the method convergence.

T a b l e 3
$T = 1500$ K; $p = 1$ atm

k	$\|r^k\|$	$\|\delta^k\|$	$G(x^k)$	$\sqrt{\Phi_k}$
7	$1.7 \cdot 10^{-13}$	$6.6 \cdot 10^5$	-769273.19269	485.23
8	$1.6 \cdot 10^{-2}$			
9	$5.0 \cdot 10^{-13}$	$3.5 \cdot 10^4$	-769939.04789	1.7228
10	$7.4 \cdot 10^{-4}$			
11	$2.6 \cdot 10^{-13}$	$7.3 \cdot 10^3$	-769941.34203	0.4996
12	$9.6 \cdot 10^{-5}$			
13	$3.5 \cdot 10^{-14}$	$8.9 \cdot 10^2$	-769941.38471	0.05711
14	$1.0 \cdot 10^{-5}$			
15	$5.6 \cdot 10^{-15}$	88.73	-769941.38517	0.007196

Blast furnace. Data of this problem was taken from [Capitani and Brown, 1987]. In Table 4 first 10 substances belong to the gaseous phase,

$n_1 = 10$. We made three refinements, the vector $x^* = (2.4 \cdot 10^{-6},\ 6.8 \cdot 10^{-3},\ 81.3,\ 6.64,\ 6.54,\ 0.46,\ 2.1 \cdot 10^{-9},\ 187.1,\ 1.7 \cdot 10^{-19},\ 7.7 \cdot 10^{-10},\ 0.0,\ 0.0,\ 0.74,\ 42.3,\ 0.0,\ 0.0)$; $\|b - Ax^*\| = 0.77818$ was obtained after 22 iterations ($l = 22$, $\bar{f} = -100$).

Analysing the values of dual discrepancies (numbers in the column δ^{22}) at 22-th iterations we see that due to (13) concentrations of condensed compounds C, $CaCO_3$, Fe_3O_4, FeO are equal to zero. We present also the vector $y^{32} = (8.3195 \cdot 10^{-9},\ 2.3291 \cdot 10^{-5},\ 2.8919 \cdot 10^{-1},\ 2.3594 \cdot 10^{-2},\ 2.2752 \cdot 10^{-2},\ 1.5862 \cdot 10^{-3},\ 7.3287 \cdot 10^{-12},\ 6.6285 \cdot 10^{-1},\ 6.2120 \cdot 10^{-22},\ 2.6938 \cdot 10^{-13})$, where $y_j^{32} = x_j^{32} \Big/ \sigma(x^{32})$, $j = 1, \ldots, n_1$.

Table 5 presents the results obtained by using refinements (12), (13) at the iterations with uneven numbers; $\|\delta_g^k\| = \left[\sum_{j=1}^{n_1} (\delta_j^k)^2\right]^{1/2}$. Here, as above, $\rho = 0.9$, values of substances are measured in moles.

T a b l e 4

$T = 1050$ K; $p = 1$ atm

Components	y	x^{22}	δ^{22}	x^{28}	δ^{28}
CH_2O	0.0	0.0071	-69872	$2.3 \cdot 10^{-6}$	-1.3149
CH_4	2.554	0.0345	-14166	$6.6 \cdot 10^{-3}$	-1.2760
CO	0.0	81.303	-0.3822	81.628	$-8.1 \cdot 10^{-5}$
CO_2	0.0	6.5895	65.082	6.6595	0.0122
H_2	0.0	6.5464	-6.8123	6.4220	0.0131
H_2O	1.775	0.2568	5021.7	0.4478	-2.7098
HCO	0.0	0.0040	-126400	$2.1 \cdot 10^{-9}$	-0.5985
N_2	187.1	187.1	0.0	187.1	0.0
O_2	20.46	0.0016	-320790	$1.7 \cdot 10^{-19}$	-2.9403
OH	0.0	0.0033	-153.520	$7.6 \cdot 10^{-11}$	-2.1867
C	85.59	0.3385	-2369.7	0.0	-2339.5
$CaCO_3$	0.1499	0.0172	-17235	0.0	-172230
CaO	0.6063	0.7390	9.3277	0.7562	$1.4 \cdot 10^{-10}$
Fe	3.527	42.303	1.6331	42.827	0.0
Fe_3O_4	13.10	0.0799	-80575	0.0	-80611
FeO	0.0	0.2842	-17073	0.0	-17083

Table 5

$T = 1050$ K; $p = 1$ atm

k	$\|r^k\|$	$\|\delta_g^k\|$	$G(x^k)$	$\sqrt{\Phi_k}$
22	$6.6 \cdot 10^{-11}$	384130	-78103014.71	8297.9
23	0.77818			
24	$1.8 \cdot 10^{-15}$	406.95	-78117984.27	81.796
25	0.01978			
26	$2.0 \cdot 10^{-14}$	40.413	-78117985.03	9.9468
27	0.00236			
28	$2.0 \cdot 10^{-14}$	4.9483	-78117985.04	1.2193

2.6 Determination of the initial approximation

Consider the following relations:

$$\sum_{j=1}^{n} a_{ij} x_j = b_i, \qquad i = 1, \ldots, m; \tag{14}$$

$$\alpha_j \leq x_j \leq \beta_j, \qquad j = 1, \ldots, n. \tag{15}$$

When

$$\alpha_j = 0, \;\; \beta_j = \infty, \qquad j = 1, \ldots, n,$$

we obtain inequalities (2). Note, that a_{ij} are arbitrary real numbers.

Let us describe the algorithm that allows determination of the feasible point or inconsistency of system (14), (15).

Starting point. It is assumed that a vector x^0 such that

$$\alpha_j < x_j^0 < \beta_j, \qquad j = 1, \ldots, n \tag{16}$$

is set. Then the calculations are performed so that at $k \geq 1$

$$\alpha_j < x_j^k < \beta_j, \qquad j = 1, \ldots, n.$$

Weighting coefficients of the affine scaling mhetod. At the k-th iteration we determine

$$\sigma_j^k = \min\Big[(x_j^k - \alpha_j)^2, \; (\beta_j - x_j^k)^2\Big], \qquad j = 1, \ldots, n. \tag{17}$$

Let D^k be such a diagonal matrix that

$$D^k = \text{diag}\ (\sigma^k),\ \sigma^k = (\sigma_1^k, \ldots, \sigma_n^k).$$

Calculation of estimates. Determine the vector $u^k = (u_1^k, \ldots, u_m^k)$. The coordinates of this point are the solution of a system of linear equations

$$B^k u = r^k, \tag{18}$$

where r^k is the imbalance vector of equations (14) in point x^k:

$$r^k = b - Ax^k;\ \ B^k = AD^kA^T. \tag{19}$$

Note that the matrix B^k is positively defined, if the rank of matrix A is equal to m.

Iterative transition. Now we determine a direction for correction of the vector x^k:

$$s^k = D^k\delta^k,\ \ \delta^k = A^Tu^k.$$

We have

$$x^{k+1} = x^k + \lambda_k s^k. \tag{20}$$

Choice of the step value. The step λ_k should be such that $\alpha < x^{k+1} < \beta$. Calculate

$$\lambda_k = \min(1,\ \lambda_k'), \tag{21}$$

$$\lambda_k' = \rho\mu_k,\ \ 0.5 \leq \rho < 1.$$

At $\lambda_k = \mu_k$ the point x^{k+1} belongs to the boundary of a set described by relations (15). ¿From (18) – (20) we obtain that $r^{k+1} = r^k(1 - \lambda_k)$.

Termination of calculations. If one of two conditions

$$\|r^k\| < \epsilon_1,\ \ \lambda_k < \epsilon_2, \tag{22}$$

is fulfilled, the calculations terminate. The first inequality in (22) shows that linear equations (14) are satisfied with a given accuracy (in this case the point x^k is considered to be feasible). If the value of the step λ_k becomes close to zero, system (14), (15) is taken to be inconsistent.

The natural change of algorithm (16) – (22) allows a series of nonlinear systems to be investigated. Such problem is given below.

3 Maximization of entropy

3.1 Problem statement

According to [Kaganovich and Filippov, 1995] let us maximize

$$S(x,T) = \sum_{j=1}^{n_1} S_j(x,T)x_j + \sum_{j>n_1} S_j^0(T)x_j, \tag{23}$$

subject to

$$Ax = b, \quad x \geq 0; \tag{24}$$

$$H(x,T) = \sum_{j=1}^{n} H_j(T)x_j = H_0; \tag{25}$$

$$\underline{T} \leq T \leq \overline{T}, \tag{26}$$

where $S_j(x,\ T) = S_j^0(T) - R\ln[px_j/\sigma(x)]$, $b = Ay$, $H_0 = H(y,\ T_{in})$.

Here the pressure p and the enthalpy $H(x,T)$ are constant, conditions (1), (2) are supplemented by nonlinear equation (25) and inequalities (26). Expression (23) contains the formula for entropy calculation. A list of substances, the vector y, p, T_{in} are initial data for the entropy model, where T_{in} — the temperature of the initial state of a thermodynamic system; n_1 — the number of gaseous phase components.

3.2 Iterative algorithm

After the iterative process described in Section 3.6 we determine such a feasible pair $(x^0,\ T_0)$ that with a given accuracy

$$Ax^0 = b, \quad \sum_{j=1}^{n} H_j(T_0)x_j^0 = H_0.$$

Besides, $x^0 > 0$, $\underline{T} < T_0 < \overline{T}$.

Let $(x^k,\ T_k)$ be a feasible vector. The vector of dual variables $u^k = (u_1^k, \ldots, u_m^k,\ u_{m+1}^k)$ is determined by solving the following system of linear algebraic equations: $B^k u = d^k$, where

$$B^k = A^k D^k (A^k)^T, \ \ d^k = -f^k D^k (A^k)^T,$$

the Jacoby matrix A^k is the matrix of first partial derivatives in point $(x^k,\ T_k)$, which is consistent with the following system of equations: $Ax =$

$b,\ H(x,\ T) = H_0$;

$f^k = (f_1^k, \ldots, f_n^k,\ f_{n+1}^k)$ is the gradient of the objective function $S(x,\ T)$ in the point $(x^k,\ T_k)$;

$D^k = \mathrm{diag}\ (\sigma_1^k, \ldots, \sigma_n^k,\ \sigma_{n+1}^k)$, $\quad \sigma_j^k = (x_j^k)^2,\ j \le n$; $\quad \sigma_{n+1}^k = \min[(T_k - \underline{T})^2,\ (\overline{T} - T_k)^2]$.

Coordinates of the vector x^{k+1} and T_{k+1} are determined by the formulas:

$$x_j^{k+1} = x_j^k + \lambda_k \sigma_j^k \delta_j^k, \quad j = 1, \ldots, n;\ \ T_{k+1} = T_k + \lambda_k \sigma_{n+1}^k \delta_{n+1}^k,$$

where

$$\delta_j^k = \sum_{i=1}^m a_{ij} u_i^k + H_j(T_k) u_{m+1}^k + f_j^k, \qquad j = 1, \ldots, n;$$

$$\delta_{n+1}^k = u_{m+1}^k \sum_{j=1}^n \frac{dH_j(T_k)}{dT} x_j^k + f_{n+1}^k.$$

As in the case above $\lambda_k = \min(\lambda_k',\ \lambda_k'')$, therewith $S(x^{k+1},\ T_{k+1}) > S(x^k,\ T_k)$. Note that it can be assumed that $\lambda_k' = 1 \Big/ \sqrt{\Phi_k}$, where $\Phi_k = \sum_{j=1}^{n+1} \sigma_j^k (\delta_j^k)^2$.

In view of nonlinear constraint (25) point $(x^{k+1},\ T_{k+1})$ frequently becomes unfeasible. In this case it is introduced into the feasible region, taking it as a starting point for the algorithm from Section 3.6. Thus, the adjustment process of a feasible solution alternates here with introduction into the feasible region.

As in Section 1 the point x^k is assumed to be feasible, if $\|r^k\| < \epsilon_1$. Here

$$r_i^k = b_i - \sum_{j=1}^n a_{ij} x_j^k, \qquad i = 1, \ldots, m;$$

$$r_{m+1}^k = H_0 - H(x^k,\ T_k),\ \ \|r^k\| = \Big[\sum_{i=1}^{m+1} (r_i^k)^2\Big]^{1/2}.$$

The equality

$$\sum_{j=1}^{n+1} f_j^k \sigma_j^k \delta_j^k = \Phi_k \ \text{ is true, if } \|r^k\| < \epsilon_1.$$

3.3 Termination of calculations

If two relations are satisfied

$$\|r^k\| < \epsilon_1, \quad \|\delta_g^k\| < \epsilon_2,$$

where $\|\delta_g^k\| = \left[\sum_{j=1}^{n_1} (\delta_j^k)^2\right]^{1/2}$, the calculations terminate.

3.4 Acceleration of the method convergence

Optimality conditions of problem (23) – (26) have the following form: there exist the feasible pair $(x',\ T')$ and the vector of Lagrangian multipliers $u' = (u_1', \ldots, u_m',\ u_{m+1}')$ such that

$$\sum_{i=1}^{m} a_{ij} u_i' + H_j(T') u_{m+1}' = -\frac{\partial S(x',\ T')}{\partial x_j}, \qquad j = 1, \ldots, n_1; \tag{27}$$

$$\frac{\partial H(x',\ T')}{\partial T} u_{m+1}' = -\frac{\partial S(x',\ T')}{\partial T}. \tag{28}$$

Besides, equalities (27) are satisfied at $j > n_1$, when $x_j' > 0$. If $x_j' = 0$ $(j > n_1)$, then

$$\sum_{i=1}^{m} a_{ij} u_i' + H_j(T') u_{m+1}' \leq -S_j^0(T').$$

Note that $x_j' > 0$ at $j \leq n_1$. Besides, note that here we have conditions of the minimum of $-S(x,\ T)$ with constraints (24) – (26).

The accuracy of fulfilment of optimality conditions (27) for determination of the equilibrium in (23) – (26) can be raised by the suggested heuristic procedure similar to that described in detail in Section 1 of this work. A sequence of dual variables is shown here to converge reliably to u', i.e. in a relatively small number of iterations l we obtain a vector u^l that is close to u'. In this case for the gaseous phase components

$$x_j^* = x_j^l \exp\ (\delta_j^l\ / R), \quad j \leq n_1. \tag{29}$$

For the condensed substances relation (13) is applied:

$$x_j^* = 0, \quad \text{if } \delta_j^l < \bar{f} < 0, \quad j > n_1. \tag{30}$$

3.5 Example

In the first problem carbon is condensed (Table 6); $p = 1$ atm, $T_{in} = 273.15$ K, $l = 18$, $\bar{f} = -10$. As far as $\delta_5^{18} = -133.4$, the carbon concentration in the equilibrium mixture is equal to zero (see (30)).

The application of the refining relations (29), (30) to studies on the entropy models allows solution to be obtained in (27), with a quite high accuracy. This is seen even though from decrease of $\|\delta_g^k\|$ in Table 7.

T a b l e 6

$T_{in} = 273.15$ K; $p = 1$ atm

Components	y	x^{18}	δ^{18}	x^{29}	δ^{29}
CO_2	0.0	0.679	32.71	1.000	$-2.0 \cdot 10^{-13}$
N_2	4.5	4.405	0.0579	4.488	$-1.4 \cdot 10^{-7}$
NO	0.0	0.191	-61.87	0.025	$9.6 \cdot 10^{-3}$
O_2	1.2	0.436	-71.09	0.188	$-8.2 \cdot 10^{-5}$
C	1.0	0.331	-133.4	0.0	-171.59

T a b l e 7

$T_{in} = 273.15$ K; $p = 1$ atm

k	$\|r^k\|$	$\|\delta_g^k\|$	$S(x^k, T_k)$	T_k
3	$9.5 \cdot 10^{-11}$	409.5	1154.1566	297.62
18	$1.1 \cdot 10^{-7}$	99.761	1468.6036	1491.3
23	$9.8 \cdot 10^{-3}$	13.588	1540.9106	2099.4
26	$1.5 \cdot 10^{-5}$	0.1943	1541.7721	2136.4
29	$7.5 \cdot 10^{-11}$	$9.6 \cdot 10^{-3}$	1541.7722	2136.598

3.6 Introduction into the feasible region

Consider relations (24) – (26). For the starting point (x^0, T_0) the strict inequalities

$$x_j^0 > 0, \quad j = 1, \dots, n; \quad \underline{T} < T_0 < \overline{T}.$$

should be satisfied. Assume that $T_0 = T_{in}$.

At the k-th iteration we solve an auxiliary problem similar to (18), (19):

$B^k u = r^k$, $B^k = A^k D^k (A^k)^T$. The imbalance vector r^k, the Jacoby matrix A^k and the diagonal matrix D^k are determined above.

We have

$$x_j^{k+1} = x_j^k + \lambda_k s_j^k, \quad j = 1, \ldots, n; \quad T_{k+1} = T_k + \lambda_k s_{n+1}^k, \tag{31}$$

where

$$s_j^k = \sigma_j^k \delta_j^k, \quad \delta_j^k = \sum_{i=1}^{m} a_{ij} u_i^k + u_{m+1}^k H_j(T_k), \qquad j = 1, \ldots, n;$$

$$s_{n+1}^k = \sigma_{n+1}^k \delta_{n+1}^k, \quad \delta_{n+1}^k = u_{m+1}^k \frac{\partial H(x^k, T_k)}{\partial T}.$$

The value of the step λ_k is determined as in (21): $\lambda_k = \min(1, \lambda_k')$. It is possible to assume

$$\lambda_k' = 1 \Big/ \sqrt{\Psi_k}, \quad \Psi_k = \sum_{j=1}^{n+1} \sigma_j^k (\delta_j^k)^2.$$

Note that

$$\sum_{i=1}^{m+1} r_i^k u_i^k = \Psi_k.$$

If $\|r^k\| < \epsilon_1$, the calculations terminate. In this case the vector (x^k, T_k) is taken to be feasible.

This algorithm may be treated as a version of the Newton method applied to system (24) – (26). Method (31) allows such an interior feasible point to be obtained that the nonlinear equation $H(x, T) = H_0$ is fulfilled with a very high accuracy.

Example. Here $T_{in} = 273.15$ K, $p = 1$ atm; all substances except carbon belong to the gaseous phase (Table 10). The calculation results are also given in Table 11, (x^3, T_3) is the interior feasible point.

Table 10

$T_{in} = 273.15$ K; $p = 1$ atm

	y	x^0	x^3
CO_2	0.0	0.375	0.1064
N_2	4.5	4.5	4.29
NO	0.0	0.375	0.412
O_2	1.2	1.2	0.887
C	1.0	1.0	0.89

Table 11

$T_{in} = 273.15$ K; $p = 1$ atm

k	$\|r^k\|$	λ_k	T_k
0	$1.14 \cdot 10^5$	1.0	273.15
1	$5.47 \cdot 10^2$	1.0	296.76
2	$3.1 \cdot 10^{-2}$	1.0	297.62
3	$9.5 \cdot 10^{-11}$		297.62

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