THE CALCULATION OF A COMPLEX CHEMICAL EQUILIBRIUM IN IDEAL GASEOUS MIXTURES

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A method was proposed for the calculation of a complex chemical equilibrium in ideal gaseous mixtures. The method is based on the determination of the minimum of the total Gibbs free energy of the system; compared with earlier methods, the determination of the initial set of mole numbers of individual components is included in the calculation scheme.

Lately, much effort has been given to the solution of complex chemical equilibria. To this purpose, a whole number of generally applicable methods was deduced, which are based on two principles. In the first case, the number of linearly independent chemical reactions is determined stoichiometrically, for each of them an equilibrium relation is then established and together with balance equations both sets are solved as a system of nonlinear equations. An advantageous method of this type was proposed by Brinkley[1,2]. The other methods are based on the determination of the total Gibbs free energy of the system. The most appropriate and used method of this type was proposed by Dantzig[2-4].

A definite disadvantage of both groups of the methods is the necessity to determine an initial set of mol numbers of individual components, which must be given as input data at the beginning of the calculation. Taking into account that the determination of this initial set of mol numbers of individual components must be in accordance with the material balance of the system, it is necessary to determine it by trial and error or to calculate it by the simplex code of the linear programming. Both of these methods are work demanding and time consuming.

As an attempt to remove this difficulty we describe here a method based also on the determination of the total Gibbs free energy, at which the determination of an initial set of mol numbers is a part of the calculation scheme. Other advantages of methods which have their origin in the determination of the minimum of the Gibbs free

energy, namely the steepness of the convergence and relatively short machine times, are conserved in this method.

FORMULATION OF THE PROBLEM

Let us consider a closed system containing N components and M elements. Each element is present in the amount of b_j gram atoms, the number of gram atoms of the j-th element in the i-th component is described by constitution coefficients a_{ij}. The chemical equilibrium of so defined system is a state, in which the total Gibbs free energy reaches a minimum. Instead of the total Gibbs free energy of the system, it is better to introduce a dimensionless quantity G/RT. The determination of the chemical equilibrium is thus equivalent to finding the minimum of the function

$$G(n_1, n_2, ..., n_N) = \sum_{i=1}^{N} n_i(c_i + \ln n_i/n) \qquad (1)$$

on the point set $(n_1, n_2, ..., n_N)$ satisfying balance relation of the form

$$\sum_{i=1}^{N} a_{ij}n_i = b_j, \quad (j = 1, 2, ..., M) \qquad (2)$$

with

$$c_i = (G^0/RT) + \ln P \qquad (3)$$

and

$$n = \sum_{i=1}^{N} n_i \qquad (4)$$

With respect to the fact that function (1) is convex the solution is unambiguous.

It is advantageous to use to the solution[5] the method of coupled extremes, (Lagrange multipliers). Let us define a function

$$K(\lambda_1, \lambda_2, ..., \lambda_M, n_1, n_2, ..., n_N) =$$

$$= G(n_1, n_2, ..., n_N) + \sum_{j=1}^{M} \lambda_j(b_j - \sum_{i=1}^{N} a_{ij}n_i) \qquad (5)$$

A point, in which function (1) reaches a minimum on set (2) must satisfy relations

$$\partial K/\partial n_s = 0; \quad (s = 1, 2, ..., N), \qquad (6)$$

$$\sum_{i=1}^{N} a_i n_{ij} = b_j; \quad (j = 1, 2, ..., M) \qquad (7)$$

Performing derivatives in Eq. (6) we obtain

$$x_i = \exp\left(\sum_{k=1}^{M} a_{ik}\lambda_k - c_i\right); \quad (i = 1, 2, \ldots, N), \tag{8}$$

where x_i is the mol fraction of the i-th component. Dividing Eq. (7) by the total number of mol in the system, substituting Eq. (8) into Eq. (7), and taking into account that the sum of the mol fractions is equal to unity we obtain

$$\sum_{i=1}^{N} a_{ij} \exp\left(\sum_{k=1}^{M} a_{ij}\lambda_k - c_i\right) - b_j t = 0; \quad (j = 1, 2, \ldots, M),$$

$$\sum_{i=1}^{N} \exp\left(\sum_{k=1}^{M} a_{ik}\lambda_k - c_i\right) = 1, \tag{9}$$

where $t = 1/n$.

It is obvious, that the solution of Eq. (9) enables us to get trivially the required result given by Eqs (1), (2), and (8).

SOLUTION OF THE SYSTEM

System (9) is a set of $(M + 1)$ equations for $(M + 1)$ unknown variables. Let us try to find its solution by the gradient method[6]. To this purpose we define a function

$$\Phi(\lambda_1, \lambda_2, \ldots, \lambda_M, t) = \sum_{j=1}^{M} \left[\sum_{i=1}^{N} a_{ij} \exp\left(\sum_{k=1}^{M} a_{ik}\lambda_k - c_i\right) - b_j t\right]^2 +$$

$$+ \left[\sum_{i=1}^{N} \exp\left(\sum_{k=1}^{M} a_{ik}\lambda_k - c_i\right) - 1\right]^2. \tag{10}$$

It is obvious that the solution of system (9) is identical with the point in which function (10) reaches its absolute minimum. In order to be able to use the gradient method, we must find such a point set Q with element $(\lambda_1, \lambda_2, \ldots \lambda_M, t)$ so that it holds
1. Q is an open continuous set; 2. $(\bar\lambda_1, \bar\lambda_2, \ldots \bar\lambda_M, t) \in Q$, where $(\bar\lambda_1, \bar\lambda_2, \ldots \bar\lambda_M, t)$ is the solution of system (9); 3. Function Φ is convex in Q; 4. The first approximation of the solution of system (9) is in Q.

The second and third conditions warrants us that set Q contains just one point in which function Φ has a local extreme and that this extreme is the absolute minimum of function Φ. The first and fourth conditions secure the convergence of the gradient method to the point $(\bar\lambda_1, \bar\lambda_2, \ldots \bar\lambda_M, t)$. Let us examine the validity of these conditions for the given case.

$$\partial^2\Phi/\partial\lambda_s^2 = 2 \sum_{j=1}^{M} \left\{\left[\sum_{i=1}^{N} a_{ij}a_{is} \exp\left(\sum_{k=1}^{M} a_{ik}\lambda_k - c_i\right)\right]^2 + \right.$$

$$+ \left[\sum_{i=1}^{N} a_{ij} \exp \left(\sum_{k=1}^{M} a_{ik}\lambda_k - c_i \right) - b_j t \right] \cdot \left[\sum_{i=1}^{N} a_{ij}a_{is}^2 \exp \left(\sum_{k=1}^{M} a_{ik}\lambda_k - c_i \right) \right] +$$

$$+ 2 \left\{ \left[\sum_{i=1}^{N} a_{is} \exp \left(\sum_{k=1}^{M} a_{ik}\lambda_k - c_i \right) \right]^2 + \right.$$

$$\left. + \left[\sum_{i=1}^{N} \exp \left(\sum_{k=1}^{M} a_{ik}\lambda_k - c_i \right) - 1 \right] \cdot \left[\sum_{i=1}^{N} a_{is}^2 \exp \left(\sum_{k=1}^{M} a_{ik}\lambda_k - c_i \right) \right] \right\} ; \quad (s = 1, 2, \ldots N) .$$

$$\partial^2 \Phi / \partial t^2 = 2 \sum_{j=1}^{M} b_j^2 . \tag{11}$$

Because $a_{ij} \geqq 0$ for all i and j, it follows from Eq. (11) that there is an $\varepsilon > 0$ that the variable set $(\lambda_1, \lambda_2, \ldots \lambda_M, t)$ fulfilling nonequalities

$$\left[\sum_{i=1}^{N} a_{ij} \exp \left(\sum_{k=1}^{M} a_{ik}\lambda_k - c_i \right) - b_j t \right] > \varepsilon ; \quad (j = 1, 2, \ldots M) ,$$

$$\left[\sum_{i=1}^{N} \exp \left(\sum_{k=1}^{M} a_{ik}\lambda_k - c_i \right) - 1 \right] > -\varepsilon , \tag{12}$$

satisfies conditions (1) − (3). The fulfillment of condition 1 follows from the fact, that the functions on the left hand sides of nonequalities (12) are monotone in all variables. The fulfillment of conditions (2) and (3) is obvious. We choose a first approximation $(\lambda_1^{(1)}, \lambda_2^{(1)}, \ldots, \lambda_M^{(1)}, t^{(1)})$ so that it holds

$$\sum_{i=1}^{N} \exp \left(\sum_{k=1}^{M} a_{ik}\lambda_k^{(1)} - c_i \right) > 1 , \tag{13}$$

$$t^{(1)} < \min \left\{ \left[\sum_{i=1}^{N} a_{ij} \exp \left(\sum_{k=1}^{M} a_{ik}\lambda_k^{(1)} - c_i \right) \right] / b_j \right\} ; \quad (j = 1, 2, \ldots, M) . \tag{14}$$

Relation (13) is easy to fulfill with respect to the fact that the coefficient a_{ik} cannot be negative. If we choose the first approximation according to (13) and (14), condition (4) will be satisfied too.

FIRST OPTIMUM APPROXIMATION

The fulfillment of conditions (13) and (14) imposed on the first approximation ensures the convergence theoretically. It is however advantageous to choose the first approximation with exploitation of the entire knowledge of the problem. Let us denote

$$p_i = \sum_{k=1}^{M} a_{ik}\lambda_k - c_i ; \quad (i = 1, 2, \ldots, N) , \tag{15}$$

$$x_i = \exp p_i ; \quad (i = 1, 2, \ldots, N) , \tag{16}$$

where x_i stand for mol fractions. It is obvious that

$$p_i < 0 ; \quad (i = 1, 2, ..., N) . \tag{17}$$

An average value of a mol fraction is $1/N$. Let us then choose a first approximation λ_k $(k = 1, 2, ..., M)$ that the function

$$F(\lambda_1, \lambda_2, ..., \lambda_M) = \sum_{i=1}^{N} \big[\sum_{k=1}^{M} a_{ik}\lambda_k - c_i - \ln(1/N) \big]^2 \tag{18}$$

be minimized. By the least the squares method we obtain values of $\lambda_k^{(1)}$ $(k = 1, 2, ..., M)$. Thus obtained values we substitute into relations (15) and (16). If the first approximation of any mol fraction is greater than unity, the by a proper diminution of the values of $\lambda_k^{(1)}$ $(k = 1, 2, ..., M)$ we obtain a new first approximation $\lambda_k^{(1')}$ $(k = 1, 2. ..., M)$ in which all x_i $(i = 1, 2, ..., N)$ are less than unity. Then with the aid of relation (14) we obtain a value of $t^{(1)}$.

ESTIMATION OF THE ERROR

Mol fractions, numbers of mol of individual components, and the Gibbs free energy of the system are functions of variables $(\lambda_1, \lambda_2, ... \lambda_M, t)$. Let us show how easy it is to estimate the error in the equilibrium composition of the system. Let us define a general differentiable function

$$z = f(\lambda_1, \lambda_2, ..., \lambda_M, t) . \tag{19}$$

Let us suppose that a vector $(\bar{\lambda}_1, \bar{\lambda}_2, ..., \bar{\lambda}_M, \bar{t})$ is an exact solution of system (9) and that the numerical calculation converged up to a vector $(\bar{\bar{\lambda}}_1, \bar{\bar{\lambda}}_2, ..., \bar{\bar{\lambda}}_M, \bar{\bar{t}})$. If we assume that both vectors are "close to each other", then it follows from the theory of errors[6] that

$$(\bar{z} - \bar{\bar{z}}) = (f(\bar{\lambda}_1, \bar{\lambda}_2, ..., \bar{\lambda}_M, \bar{t}) - f(\bar{\bar{\lambda}}_1, \bar{\bar{\lambda}}_2, ..., \bar{\bar{\lambda}}_M, \bar{\bar{t}})| \leqq$$

$$\leqq \sum_{k=1}^{M} \Big| \frac{\partial f}{\partial \lambda_k} \Big| \varepsilon_k + \Big| \frac{\partial f}{\partial t} \Big| \varepsilon_t , \tag{20}$$

where ε_k $(k = 1, 2, ..., M)$ is the maximum absolute error in λ_k $(k = 1, 2, ..., M)$. ε_t is then the maximum absolute error in t. The values of derivatives are evaluated in the point $(\bar{\bar{\lambda}}_1, \bar{\bar{\lambda}}_2, ..., \bar{\bar{\lambda}}_M, \bar{\bar{t}})$. If we assume that the numerical calculation allows us to estimate the error in the values of $\lambda_1, \lambda_2, ..., \lambda_M, t$, then it holds for example for mole fraction (16)

$$(x_i - x_i^{(n)}| \leqq x_i^{(n)} \sum_{s=1}^{M} a_{is}\varepsilon_s ; \quad (i = 1, 2, ..., N) , \tag{21}$$

where $x_i^{(n)}$ is the n-th approximation of the exact value of x_i. Similar estimations of errors may be obtained analogically for both individual components and the Gibbs free energy.

Description of the Gradient Method

The gradient method is described in detail in many textbooks on numerical methods[6]. Therefore in the following only the most necessary relations will be given, which we need in the connection with the use of our method.

Let be given a system

$$
\begin{aligned}
f_1(x_1, x_2, \ldots, x_N) &= 0 , \\
f_2(x_1, x_2, \ldots, x_N) &= 0 , \\
&\vdots \\
f_N(x_1, x_2, \ldots, x_N) &= 0 .
\end{aligned}
\tag{22}
$$

Let us define a function

$$
U(x_1, x_2, \ldots, x_N) = \sum_{i=1}^{N} f_i^2(x_1, x_2, \ldots, x_N) .
\tag{23}
$$

The solution of (22) is equivalent to finding a point $\bar{x} = (\bar{x}_1, \bar{x}_2, \ldots, \bar{x}_N)$ in which function (11) reaches its absolute minimum. A vector

$$
(-\partial U/\partial x_1 , \quad -\partial U/\partial x_2, \ldots, \quad -\partial U/\partial x_N)
\tag{24}
$$

determines the direction of the steepest descent of function (23) in an arbitrary point $x = (x_1, x_2, \ldots, x_N)$, in which the function is defined and in which all its first partial derivatives are continuous. Let us construct a function

$$
\psi(K) = U\left(x_1^{(1)} - K \frac{\partial U}{\partial x_1} , \ldots, x_N^{(1)} - K \frac{\partial U}{\partial x_N}\right),
\tag{25}
$$

where

$$
\frac{\partial U}{\partial x_i} = \left(\frac{\partial U}{\partial x_i}\right)_{x = x^{(1)}} .
\tag{26}
$$

Function $\psi(K)$ determines changes of function U in the direction of the steepest descent in the point $x^{(1)}$. We establish a value of the coefficient $K = K_1$ that function $\psi(K)$ reaches its minimum at K_1. Now let us write

$$
d\psi(K)/dK = 0 .
\tag{27}
$$

The lowest positive root of Eq. (27) determines the K_1. The second approximation will be chosen according to

$$
x_i^{(2)} = x_i^{(1)} - K_1 \left(\frac{\partial U}{\partial x_i}\right)_{x = x^{(1)}} ; \quad (i = 1, 2, \ldots, N) .
\tag{28}
$$

Eq. (27) will be solved either numerically or we use the method of the approximate determination of the coefficient K_1 (cf.[6]). With respect to the slow convergence of the gradient method it is optimal to use it only to obtain the first approximation. If the check proves that it is possible

to continue further by the Newton method, the solution of system (22), resp. (9), will be accomplished in this way.

During the application of the Newton method on system (9) it is important that the values of mol fractions (8) be kept after each step of the Newton method in the interval ⟨0·1⟩. This may be easily achieved by choosing the $(i + 1)$th approximation of the solution of the system that

$$\lambda_j^{(i+1)} = \lambda_j^{(i)} + \varepsilon\,\Delta\lambda_j^{(i)} \quad (j = 1, 2, ..., M) \tag{29}$$

$$t^{(i+1)} = t^{(i)} + \varepsilon\,\Delta t ,$$

where $\Delta\lambda_1^{(i)}, \Delta\lambda_2^{(i)}, ..., \Delta\lambda_M^{(i)}, \Delta t^{(i)}$ are increments of the values of $\lambda_1^{(i)}, \lambda_2^{(i)}, ..., \lambda_M^{(i)}, t^{(i)}$ obtained in the i-th step of the Newton method. The value of $\varepsilon \in \langle 0·1\rangle$ will be chosen so that it holds $x_i \in \langle 0·1\rangle$ $(i = 1, 2, ..., N)$ after substituting Eq. (29) into (8).

TABLE I

Results of the Calculation of the Chemical Equilibrium of the Combustion of Propane by Air at $2200°K$ and 40 atm, (ratio of $O_2 : N_2$ in Air to be 1 : 4)

Component	$-(G° - H_0°)/T$	$H_0°$	Number of mol of individual components		Upper estimate of the error
			Dantzig	this work	
H	32·353	+51 620	0·000 667	0·000 668	$(1·2) . 10^{-11}$
H_2	38·364	0	0·020 807	0·020 808	$(7·4) . 10^{-11}$
O	43·488	+58 586	0·000 445	0·000 446	$(4·8) . 10^{-13}$
O_2	56·586	0	0·033 712	0·033 727	$(3·8) . 10^{-10}$
OH	51·129	+10 000	0·015 710	0·015 709	$(4·2) . 10^{-10}$
H_2O	54·263	−57 104	3·971 006	3·971 000	$(1·8) . 10^{-7}$
CO	54·826	−27 202	0·081 294	0·081 328	$(1·7) . 10^{-9}$
CO_2	63·012	−93 969	2·918 706	2·918 688	$(6·5) . 10^{-8}$
N_2	53·220	0	19·986 644	19·986 655	$(8·2) . 10^{-7}$
NO	58·005	+21 477	0·026 713	0·026 712	$(6·8) . 10^{-10}$
n	—	—	27·056 371	27·055 741	$(2·4) . 10^{-7}$
G	—	—	—	−77·4969	$(2·9) . 10^{-5}$

EXAMPLE

To illustrate the method an example was chosen, which was used previously for checking some earlier methods of calculations of complex equilibria, namely the combustion of propane by a stoichiometrical amount of air at $2200°K$ and 40 atm. It has been assumed the oxidation proceeds that quantitatively, that the reaction mixture contains H, H_2, O, O_2, OH, H_2O, CO, CO_2, N_2, and NO, and that the mixture behaves ideally. Input data for G-functions and $H_0°$ values of individual components, which were calculated by a numerical interpolation from tabulated values at 2000, 2250, and $2500°K$ [7], are given in first two columns of Table I. In further columns of this table, results of our calculation are compared with those calculated earlier by the method of White,

Johnson, and Dantzig[4]. Results of calculations of other authors[8,9] are not included as they are less accurate by several orders and moreover they were surveyed in a tabular form in an earlier work[4]. From the table we may judge on a high accuracy of the calculation and good agreement with the results of the so far wide spread Dantzig method is obvious.

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