CALCULATION OF CHEMICAL EQUILIBRIUM IN COMPLEX SYSTEMS: SYSTEM RESTRICTIONS

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Dedicated to Professor Ľudovít Treindl on the occasion of his 70th birthday.

The set of positive solutions of the mass balance equations Ω must not be empty; otherwise, at least one species exists which has zero number of moles independently of the chemical changes in the system. If the set Ω is empty, then numerical problems can occur in the course of the calculation of chemical equilibrium. Two examples demonstrate the importance of this problem and the algorithm, allowing to prove emptiness or non-emptiness of the set Ω, is proposed.
Key words: Thermodynamics; Chemical equilibria; Gibbs energy; Mass balance equations; Non-stoichiometric methods.

The determination of chemical equilibrium of a closed system at a given temperature, pressure and feed composition is one of the most important calculation problems in applied chemical thermodynamics. The calculation methods are usually based on the solution of a set of equilibrium conditions (each condition corresponds to one considered independent chemical reaction) for the set of points satisfying stoichiometric mass balance equations or on the minimization of the Gibbs energy for the set of points satisfying non-stoichiometric mass balance equations[1–10]. The first set of methods (stoichiometric methods) is usually used for determination of the chemical equilibrium of a simple (small) system. For determination of a complex (large) system having many species and phases, the minimization technique of the Gibbs energy is often used (non-stoichiometric methods). Non-stoichiometric methods (for example the second-order RAND algorithm) have the following advantages: (i) stoichiometric analysis of the system need not be done, (ii) easier numerical process in the case of a large

system. On the other hand, using non-stoichiometric methods (*i.e.,* absence of any stoichiometric analysis) brings several problems. Some of them were already discussed in literature (so-called numerical singularities, see Smith and Missen[3], Chap. 9.2). The equilibrium conditions are derived under the assumption that the set Ω of positive solutions of the mass balance equations is not empty, *i.e.*, starting from the initial substances, the non-zero amounts of all species in the system can be obtained. The case $\Omega = \{\emptyset\}$ (*i.e.*, the set Ω is empty) is typical of non-stoichiometric methods where the system is defined only by the choice of the formula matrix $\boldsymbol{A}$ and no stoichiometric analysis is done. The importance of this problem will be demonstrated in this paper and methods (i) of proving $\Omega = \{\emptyset\}$ and (ii) of finding a positive solution will be proposed. The denotation "system restriction" is chosen in accordance with Smith and Missen[2] and Cheluget *et al.*[11].

THEORETICAL ANALYSIS

Let us consider an isothermal and isobaric closed system where no work other than that related to volume change (pressure–volume work) is involved. The determination of chemical equilibrium in such a system at constant temperature T and pressure p is equivalent to the finding of a point of global minimum of the total Gibbs energy G

$$\min G; \qquad G = \sum_{i=1}^{N} n_i \mu_i \qquad (1)$$

on the set of points $(n_1, n_2, \ldots, n_N)$ satisfying the non-stoichiometric mass balance equations

$$\sum_{i=1}^{N} a_{ji} n_i = b_j; \quad j = 1, 2, \ldots, M$$
$$n_i \geq 0; \quad i = 1, 2, \ldots, N, \qquad (2)$$

where M is the number of chemical elements which the system is composed of and N is the number of species. The chemical species is a chemical entity distinguishable from other entities by its molecular formula or by its molecular structure or by the phase in which it occurs. Matrix $\boldsymbol{A} = \{a_{ji}\}$ is the matrix of constitution coefficients (formula matrix) where a_{ji} is the number of atoms of the j-th element in the molecule (or in the formula unit) of the i-th species, b_j is the total (fixed) amount of moles of the j-th element and is

determined from the initial (feed) composition, n_i and μ_i are the number of moles and chemical potential of the i-th species in the given phase, respectively. We always assume $N > M$ and

$$\text{rank}(\boldsymbol{A}) = M . \tag{3}$$

If rank($\boldsymbol{A}$) < M then the linearly dependent rows of the matrix $\boldsymbol{A}$ are removed and the new value of M, $M = \text{rank}(\boldsymbol{A})$ is considered. Equation (4) holds

$$R_{\max} = N - \text{rank}(\boldsymbol{A}) , \quad \textit{i.e.} \quad R_{\max} = N - M , \tag{4}$$

where $R_{\max}$ is the maximum number of independent chemical reactions in the system.

Let us consider an arbitrary multicomponent phase which has a non-zero number of moles in equilibrium. All species of such multicomponent phase (which are products of chemical changes starting from initial substances) satisfy the following conditions in equilibrium (see ref.[3], p. 47 or ref.[9])

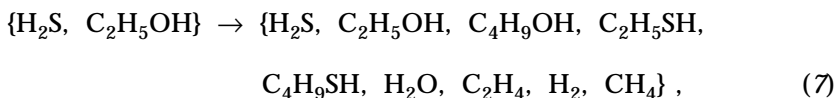$$\mu_i = \mu_i^0 + RT \ln a_i = \sum_{k=1}^{M} a_{ki} \lambda_k ; \quad i = 1, 2, \ldots, \tag{5}$$

where μ_i^0 is the chemical potential of the i-th species in the standard state, λ_k, $k = 1, 2, \ldots, M$ are unknown Lagrangian multipliers and a_i is the activity of the i-th species (*i.e.*, each species has a non-zero activity and therefore a non-zero number of moles in equilibrium). The equilibrium conditions (Eq. (5)) also hold for single species phases if they are present in the equilibrium. A suitable combination of equilibrium relations (Eq. (5)) and mass balance equations (Eq. (2)) gives the non-stoichiometric numerical process for determination of the chemical equilibrium of the system under consideration. The equilibrium conditions (Eq. (5)) are derived under the assumption that the set Ω

$$\Omega = \{\boldsymbol{n} \,|\, \boldsymbol{n} > 0 , \ \boldsymbol{A}\boldsymbol{n} = \boldsymbol{b}\} \tag{6}$$

is not empty ($\boldsymbol{n} > 0$ means $n_i > 0$ for all $i = 1, 2, \ldots, N$). The set Ω is a set of all positive solutions of the mass balance equations $\boldsymbol{A}\boldsymbol{n} = \boldsymbol{b}$ where $\boldsymbol{n} =$

$(n_1, n_2, ..., n_N)$ and $\mathbf{b} = (b_1, b_2, ..., b_M)$ are column vectors. If the set Ω is empty (*i.e.*, no positive solution exists) then at least one species has zero number of moles independently of the chemical changes in the system. Such species is called the "underivable" species because it is not possible to "derive" such a species from initial species. The set of equations $\mathbf{An} = \mathbf{b}$ has always a non-negative solution which is equal to the initial (feed) composition. In general, the existence of the positive solution is not guaranteed and depends on the formula matrix $\mathbf{A}$ and on the initial composition of the system.

Let us demonstrate that considering the homogeneous system

$$\{H_2S, \ C_2H_5OH\} \rightarrow \{H_2S, \ C_2H_5OH, \ C_4H_9OH, \ C_2H_5SH,$$

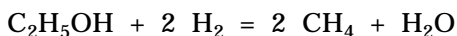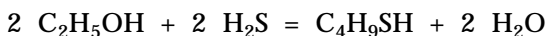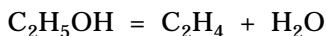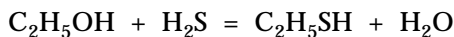$$C_4H_9SH, \ H_2O, \ C_2H_4, \ H_2, \ CH_4\} \,, \tag{7}$$

where the curly brackets on the left contain initial species and the system is defined by the species between the curly brackets on the right. $N = 9$, rank($\mathbf{A}$) = M = 4 and R_{max} = 5. Let the initial mixture contain 1 mol of hydrogen sulfide and α mol of ethanol. The mass balance equations (Eq. (2)) have the following form

$$2n_1 + 6n_2 + 10n_3 + 6n_4 + 10n_5 + 2n_6 + 4n_7 + 2n_8 + 4n_9 = 2 + 6\alpha$$

$$2n_2 + 4n_3 + 2n_4 + 4n_5 \qquad + 2n_7 \qquad + n_9 = \qquad 2\alpha$$

$$n_2 + n_3 \qquad\qquad + n_6 \qquad\qquad\qquad = \qquad \alpha \tag{8}$$

$$n_1 \qquad\qquad + n_4 + n_5 \qquad\qquad\qquad\qquad = 1$$

being the mass balance for H, C, O and S, respectively. Using the Gaussian algorithm, we can rewrite Eq. (8) into the equivalent form.

$$n_1 = 1 - n_4 - n_5$$

$$n_2 = \alpha + n_4 + 2n_5 - n_6 + n_7 + 0.5n_9$$

$$n_3 = \qquad - n_4 - 2n_5 + n_6 - n_7 - 0.5n_9 \tag{9}$$

$$n_8 = \qquad\qquad\qquad\qquad - n_9$$

It follows from the last equation that the conditions n_8, $n_9 \geq 0$ are satisfied only if $n_8 = n_9 = 0$, *i.e.*, the set Ω is empty. The explanation follows from the stoichiometric analysis. The chemical changes in the system are described by five independent reactions. Let us write them in such a form that the initial species are on the left-hand sides of the chemical reactions.

$$C_2H_5OH \ + \ H_2S \ = \ C_2H_5SH \ + \ H_2O$$

$$C_2H_5OH \ = \ C_2H_4 \ + \ H_2O$$

$$2 \ C_2H_5OH = C_4H_9OH \ + \ H_2O \qquad (10)$$

$$2 \ C_2H_5OH \ + \ 2 \ H_2S \ = \ C_4H_9SH \ + \ 2 \ H_2O$$

$$C_2H_5OH \ + \ 2 \ H_2 \ = \ 2 \ CH_4 \ + \ H_2O$$

Hydrogen and methane occur only in the fifth reaction on the opposite sides. Therefore, hydrogen and methane are "underivable" from the initial species in the system under consideration. Chemical potentials of hydrogen and methane are equal to minus infinity and therefore they cannot be equal to the linear combinations of Lagrangian multipliers (see Eq. (*5*)); numerical problems can occur in the course of the calculation. If we include, for example, acetylene C_2H_2 into the system (*7*), then the set Ω is not empty because acetylene and hydrogen are products of dehydrogenation of ethene

$$C_2H_4 \ = \ C_2H_2 \ + \ H_2 \qquad (11)$$

occurring on the same side of the chemical equation. Therefore, including acetylene C_2H_2 into the system (*7*) seems to be a natural extension of the system (*7*) guaranteeing the non-emptiness of the set Ω. From the numerical point of view, this is true only if acetylene is "sufficiently" thermodynamically stable for given reaction conditions (temperature, pressure and feed composition). If not, *i.e.*, if the equilibrium mixture contains only a "small" amount of acetylene, then the equilibrium mixture contains also only "small" amounts of hydrogen and methane. In such a case, rank(A^*) < 4 where A^* is the formula matrix containing only species having "sufficient" amount of moles in equilibrium. The case rank(A^*) < rank(A)

(so-called numerical singularity) brings many numerical problems (see ref.[3], Chap. 9.2).

Still there is one important reason why we must be able to find whether the set Ω is empty or not. The calculation of chemical equilibrium of the multicomponent heterogeneous system is based on the consecutive exclusion and inclusion of phases from and into the numerical process until the system is thermodynamically stable with respect to phases not included in the system (see ref.[9]). Usually the model of a totally immiscible system is used for the determination of the first approximation of a chemical equilibrium calculation at given temperature, pressure and feed composition[2,10,12,13]. In such a case, the relation (*1*) has the following form

$$\text{min } G^*; \qquad G^* = \sum_{i=1}^{N} n_i \mu_i^* \ , \tag{12}$$

where $\mu_i^* = \mu_i^0 + \alpha RT \ln (p/p_{st})$, p_{st} is the standard pressure and $\alpha = 0$ or 1 for condensed or gaseous species, respectively. Because μ_i^* is a constant at given temperature and pressure, the Gibbs energy G^* of the totally immiscible system is a linear function of number of moles n_i, $i = 1, 2, ..., N$. The well-known simplex algorithm can be used to solve Eqs (*12*) and (*2*). The simplex method gives a set of M basic species having non-negative number of moles and other species having zero number of moles[14]. These M basic species have usually positive numbers of moles and only in a special (so-called degenerate) case, some of the basic species have zero numbers of moles. Therefore the vector $\boldsymbol{n} = (n_1, n_2, ..., n_N)$ solving Eqs (*12*) and (*2*) has at most M positive components. The first approximation of the equilibrium state contains only such phases in which at least one basic species is present. Such an obtained set of phases evidently satisfies the Gibbs phase rule $F \geq M$ for arbitrary but fixed values of temperature and pressure, where F is number of phases in equilibrium. As it was mentioned above, the calculation method is based on the consecutive exclusion and inclusion of the phases from and into the numerical process (starting from the first approximation usually obtained from the model of totally immiscible phases). Therefore, we have to test the condition $\Omega \neq \{\emptyset\}$ for all subsystems which occur in the course of the numerical process. Let us demonstrate this considering the following simple case:

$$\{AlCl_3, AsH_3, H_2\} \rightarrow \{AlCl_3, AsH_3, H_2, As_2, As_4, HCl, AlAs(s)\} \ , \tag{13}$$
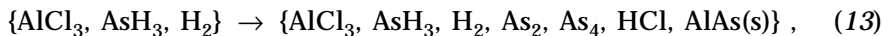
where $N = 7$, rank(A) $= M = 4$, $R_{max} = 3$ and all species (with the exception of the solid AlAs) belong to the gaseous phase. Independent chemical reactions describing chemical changes in the system may have the following form.

$$4 \; AsH_3 = AsH_4 + 6 \; H_2$$

$$As_4 = 2 \; As_2 \qquad (14)$$

$$AlCl_3 + AsH_3 = 3 \; HCl + AlAs(s)$$
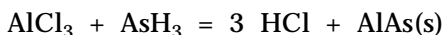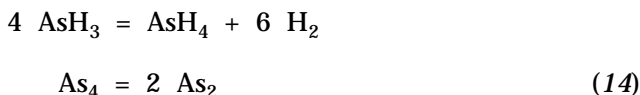
The values important for the above-mentioned demonstration are summarized in Table I. The fourth column contains the results of the simplex method (model of a totally immiscible system). The basic species are $AlCl_3$, H_2, As_4 and HCl where HCl is the basic species having zero number of moles. Because all basic species belong to the gaseous phase, the first approximation contains only the gaseous phase. And here lies the essence of the problem. The set Ω is not empty for the whole system (13) but it is empty for the subsystem containing only the gaseous phase because it is not possible to "derive" HCl from the input species in the gaseous phase. In this case, the model of a totally immiscible system does not give an acceptable first approximation.

TABLE I
Input and equilibrium data of the system (13) at temperature 1 000 K and standard pressure 101.3 kPa

Species	μ^0(1 000 K)[a] kJ mol^{-1}	Input amount mol	First approximation mol	Equilibrium amount mol
$AlCl_3$(g)	−938.149	1	1	0.9658
AsH_3(g)	−181.169	10	0	0.0008
H_2(g)	−145.516	99	114	113.9
As_2(g)	−68.478	0	0	0.1552
As_4(g)	−214.894	0	2.5	2.414
HCl(g)	−294.133	0	0	0.1026
AlAs(s)	−200.441	0	0	0.0342

[a] Ref.[15]

PROPOSED ALGORITHMS

It follows from linear algebra and the above discussed examples that it is not easy to decide whether the set of mass balance equations (*2*) has a positive solution or not. Probably, it is not possible to expect the existence of a simple method containing only a few numerical steps. The proposed method consists of two simultaneously running algorithms: (i) the first algorithm searches for a species which is not "derivable" from the initial substances, *i.e.*, the set Ω is empty if such a species is found; (ii) the other algorithm creates a positive solution using the method of basic species, *i.e.*, the set Ω is not empty if such a solution is created.

The proposed process consists of several steps. The general *k*-th step $k = 1$, 2, 3, ... has the following form:

1) Let us choose *M* species which are characterized by the vector of indexes $\boldsymbol{I}^{(k)} = (i_1, i_2, ..., i_M)$, $\boldsymbol{I}^{(k)} \neq \boldsymbol{I}^{(k-j)}$, $j = 1, 2, ..., k - 1$ where $\boldsymbol{A}_I$ is the constitution (formula) matrix composed of *M* chosen species (*i.e.*, $\boldsymbol{A}_I$ is a square matrix of the order *M*). Without loss of generality, we assume $1 \leq i_1 < i_2 < ... < i_M \leq N$.

2) If $\boldsymbol{A}_I$ is a singular matrix, then $k \leftarrow k + 1$ and we go back to point 1.

3) The considered set of *M* species forms a set of basic species (see Appendix). Using the well-known Gaussian algorithm we rewrite the set of mass balance equations (Eq. (*2*)) into the equivalent form

$$n_{i_j} = d_j + \sum_{s \notin \boldsymbol{I}^{(k)}} c_{js} n_s ; \quad j = 1, 2, ..., M \tag{15}$$

(see Eq. (*9*) where $\boldsymbol{I} = (1, 2, 3, 8)$).

4) Let exist an index *j* with the following properties

$$d_j \leq 0 \quad \text{and} \quad c_{js} \leq 0 \quad \text{for all} \quad s \notin \boldsymbol{I}^{(k)} . \tag{16}$$

In such a case, the numerical process is finished because $n_{ij} = 0$ independently of the chemical changes in the system and therefore the set Ω is empty.

5) If $d_j > 0$ for all $j = 1, 2, ..., M$, then the numerical process is also finished because the set Ω is not empty (see Appendix).

6) If $d_j \geq 0$ for all $j = 1, 2, ..., M$ (*i.e.*, at least one d_j is equal to zero), then

$$x_{i_j} \leftarrow x_{i_j} + d_j \; ; \quad j = 1, \, 2, \, \ldots, \, M \, , \qquad (17)$$

where $\boldsymbol{x}$ is N-dimensional vector having at the beginning of the numerical process all components equal to zero (the vector $\boldsymbol{x}$ is sum of non-negative solutions of the set of equations (2)). The value of ω increased, $\omega \leftarrow \omega + 1$, where integer ω is also equal to zero at the beginning of the numerical process.

7) If $x_i > 0$ for all $i = 1, 2, \ldots, N$, then the vector $\boldsymbol{n} = \boldsymbol{x}/\omega$ is a positive solution of the set of equations (2) (the average of the solutions of the set of equations (2) is obviously also a solution of the considered set). The numerical process is finished because the set Ω is not empty.

8) $k \leftarrow k + 1$ and we go back to point 1.

It is well known from the combinatorial analysis that $k \leq \beta$ where β is equal to the binomial coefficient $^N C_M = N!/M!/(N - M)!$. The value of β can be very large but, in accordance with our experience, the numerical process is stopped relatively soon either in point 4 (if the set Ω is empty) or in point 5 (or 7) (if the set Ω is not empty). Especially in the first case (the set Ω is empty), the numerical process is usually stopped when the sequence number of an "underivable" species is for the first time considered as a component of vector $\boldsymbol{I}$.

If the model of totally immiscible system is used for the determination of the first approximation, then the result of the simplex method (number of moles of basic species) can be often used to decide whether the set of equations $\boldsymbol{An} = \boldsymbol{b}$ has a positive solution or not (see Appendix).

CONCLUSION

A relatively simple algorithm allowing to prove the existence or non-existence of a positive solution of the mass balance equations is proposed. The importance of such problem for chemical equilibrium calculations is demonstrated in detail by two practical examples.

SYMBOLS

A, a_{ij}	matrix of constitution coefficients (formula matrix) and its elements
a_i	activity of the i-th species
b, b_j	vector of the right-hand side of the mass balance equations and its j-th element
c_{j}, d_j	auxiliary coefficients
F	number of phases in equilibrium

G	Gibbs energy
I	vector of indexes
M	number of rows of the matrix A
n, n_i	vector of numbers of moles and its i-th species
N	number of species, number of columns of the matrix A
p	pressure
R_{max}	maximum number of independent reactions in the system
R	universal gas constant
T	absolute temperature
μ_i (μ_i^0)	chemical potential of the i-th species (in the standard state)
λ_k	Lagrangian multiplier corresponding with the k-th row of the matrix A
Ω	set of positive solutions of $An = b$
ω	auxiliary integer

APPENDIX

Basic Species

If A_I is a regular matrix, then the set of M species characterized by the vector $I = (i_1, i_2, ..., i_M)$ is called the set of basic species (chemical pseudo-elements, components, chemical "building blocks", *etc.*). Let α be a number of sets of basic species in the given system. The inequality $\alpha \leq {}^N C_M$ obviously holds. Because rank$(A) = M$, it must exist at least one vector I for which the matrix A_I is regular, *i.e.*, $\alpha \geq 1$. Mostly $\alpha \gg 1$ because for an arbitrary but fixed chosen species, at least one set of basic species, in which the considered species is present, exists. Therefore the number of moles of each species is at least once present on the left-hand side of the set of equations (*15*). Let us consider, for example, the system (*7*). In such case, ${}^9 C_4 = 126$ but $\alpha = 36$ because each set of basic species must contain hydrogen or methane and, obviously, must not contain simultaneously all species taking part in an arbitrary but fixed chosen chemical reaction (*10*).

Let us consider the set of equations $An = b$ where rank$(A) = M$, M is the number of equations, $n = (n_1, n_2, ..., n_N)$, $b = (b_1, b_2, ..., b_M)$ and $M < N$. The vector b is determined from the initial (feed) mixture, *i.e.*, the set $An = b$ has a non-negative solution n^0, $n^0 \geq 0$. If the considered set of equations has one positive solution $n^{(p)}$, then the set Ω has infinite number of positive solutions. This follows in general case from the properties of the continuous function defined by Eq. (*15*). In addition, it is obvious that the vector $\beta n^0 + (1 - \beta) n^{(p)}$ is the positive solution for all $\beta \in \langle 0; 1 \rangle$.

The algorithm proposed in the main text is based on the following theorem: If the set of equations $A_I d = b$ has the positive solution d for at least

one set of basic species characterized by the vector I, then the set of equations $An = b$ has a positive solution n.

Proof: If coefficients d_j ($j = 1, 2, ..., M$) from Eq. (15) are positive, then the numbers of moles of basic species on the left-hand side are obviously also positive for sufficiently small positive numbers of moles of non-basic species on the right-hand side of Eq. (15).

The inverse theorem (*i.e.*, if the set of equations $An = b$ has a positive solution, then the polyhedron defined by the set of equations $An = b$ and inequalities $n \geq 0$ has at least one non-degenerate vertex) does not hold in all cases. It is possible to find singular cases when the set of equations (2) has a positive solution but the above mentioned polyhedron has only degenerate vertices. Let us consider, as an example, a simple system $\{CO, H_2O\} \rightarrow \{CO, H_2O, CO_2, H_2\}$ where $M = 3$ and only one chemical reaction $CO + H_2O = CO_2 + H_2$ takes place. Let CO and H_2O have the same number of moles in the initial mixture. In such a special case, the system contains either two or four species but never only three of them. Points 6 and 7 in the proposed algorithm make it possible to solve such singular cases.

It follows from the theorem that if the set Ω is empty, then at least one "underivable" species having zero number of moles must be present in an arbitrary set of basic species (and therefore also in the set of basic species solving the problem of Eqs (12) and (2)). On the other hand, if the vector n solving the problem of Eqs (12) and (2) has less than M positive components, then this does not mean that the set Ω is empty. Let us consider a very simple one-phase system $\{H_2O\} \rightarrow \{H_2O, H_2, O_2\}$ and reaction conditions guaranteeing great thermodynamic stability of water. In such a case, the set of basic species solving the problem of Eqs (12) and (2) is $\{H_2O, H_2\}$ or $\{H_2O, O_2\}$ where the second species has always zero number of moles. The third set of basic species $\{H_2, O_2\}$ where both species have positive numbers of moles is not the solution of the problem of Eqs (12) and (2).

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