CONTRIBUTION TO THE WHITE–JOHNSON–DANTZIG METHOD OF CALCULATION OF THE EQUILIBRIUM COMPOSITION OF MULTICOMPONENT SYSTEMS IN THE GASEOUS PHASE

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A simple general method is proposed for the choice of the first approximation for calculating the equilibrium composition of a multicomponent system in the gaseous phase by the White––Johnson–Dantzig method. The method is used for calculating the composition of dissociation and ionization products of SF_6 on the assumption of the ideal behaviour at temperatures of 1 000 to 20 000 K and pressures of 0·1—2·0 MPa.

Commonly employed methods for calculating the chemical composition of an ideal gaseous mixture start from the knowledge of equilibrium constants of probable reactions and the stoichiometric analysis[1,2] or they are based on the minimization of the total Gibbs free energy of all components of the system considered provided that the G-functions and corresponding enthalpies of formation are known[3]. Advantages and drawbacks of contemporary calculation methods are critically evaluated in monographs[4–6] and methods for calculating the properties of real mixtures of real gases have also been elaborated[7].

A growing interest in the use of high temperatures and heat flows for chemical syntheses imposes further demands on methods for calculating the properties of equilibrium states, because, at high temperature, the systems contain besides neutral molecules and atoms also free radicals and, due to the existence of ionization processes, ions and free electrons[8,9] In the last years, the attention is being given to diagnostic problems of the so-called low-temperature plasma not only from the point of view of chemical technology, but above all in the area of the solution to basic problems of the magnetoplasmodynamic conversion of energy, physico-chemical processes in electric discharges and the effect of the discharge on the dielectric strength of gaseous media in electric devices.

At present, the White–Johnson–Dantzig (WJD) method is one of the most often employed methods for computer calculations of complex equilibria in the gaseous phase. A definite disadvantage of the WJD method is the requirement imposed on the first approximation which must satisfy balance conditions and which is necessary at the beginning of the calculation.

It is the aim of this work to describe a simple general method for the choice of the first approximation for a system in the gaseous phase on the assumption that the rank of the constitutional matrix is equal to the number of present elements.

The total enthalpy of a mixture of N components $S_1, S_2, \ldots, S_N$ containing n_i mol of the i-th component S_i can be expressed as a function of variables n_i

$$F(n_1, n_2, ..., n_N) = \sum_{i=1}^{N} f_i, \tag{1}$$

where[5]

$$f_i = n_i[c_i + \ln(n_i/n)] \tag{2}$$

$$c_i = \frac{1}{R}\left(\frac{G^0 - H_0^0}{T}\right)_i + \frac{1}{RT}(\Delta H_0^0)_i + \ln P - 11{\cdot}52608844,$$

in which values of $-[(G^0 - H_0^0)/T]_i$ and $(\Delta H_0^0)_i$ are tabulated; P is the total pressure in Pa and

$$n = \sum_{i=1}^{N} n_i.$$

For the determination of the equilibrium composition of the system it is necessary to find such positive numbers n_i, $i = 1, 2, ..., N$, which minimize Eq. (1) and satisfy the M mass balance conditions:

$$\sum_{i=1}^{N} a_{ij}n_i = b_j, \quad j = 1, 2, ..., M, \tag{3}$$

where M is the number of different elements $P_1, P_2, ..., P_M$ which make up the components $S_1, S_2, ..., S_N$; a_{ij} is the number of atoms of the element P_j in the component S_i and b_j is the total number of mol of the element P_j in the system. Thus, the system is described through elements P_j and components S_i. Numbers a_{ij}, *i.e.*, elements of the constitutional matrix,

$$\mathbf{A} = \begin{bmatrix} a_{ij} \end{bmatrix} \begin{matrix} i = 1, 2, ..., N \\ j = 1, 2, ..., M \end{matrix}$$

are determined by the components. In the WJD method for the minimization of function (1) at conditions (3), function (1) is replaced with the quadratic approximation. The equilibrium composition is then calculated by the method of subsequent approximations, which is described *e.g.* in monographs[3-6]. At the beginning of the calculation, it is necessary to choose a first approximation $n_1^{(1)}, n_2^{(1)}, ..., n_N^{(1)}$ to the final solution $n_1, n_2, ..., n_N$. Due to relation (2), the first approximation may contain only positive numbers and it must also satisfy the balance conditions (3). The calculation method then guarantees that the amounts of substances are positive for all subsequent approximations and that any subsequent approximation satisfies conditions (3). In a computer calculation, the two following circumstances must be considered. There is a certain minimal number, z, which is represented in a computer as a non-zero

number and all numbers which are less than z are represented by zeros. The representation of real numbers has a definite accuracy, the number of figures in the mantissa, c, can reach $8-12$ decimal numbers. If numbers b_j are approximately units, then, due to inaccuracies in the computer representation of real numbers, the right- and left-hand sides of condition (3) may differ from one another by approximately 10^{-c}. It can be shown that this violation of conditions (3) has no effect on the result. Consequently, it is obvious that in the calculation we cannot consider components for which the value of n_i is less than z. If it holds $n_i < z$ for some component, then, starting from a certain approximation $n_i^{(k)}$, a situation arises in which $n_i^{(k)}$ differs only little from z and the mass amount of the ith component does not change in subsequent approximations, since it must be positive, i.e., greater or equal z. Concentrations of other components can change in this instance further, however, the convergence of the series of subsequent approximations becomes extremely slow. From this reason it is suitable to select a number z_1 which would be slightly greater than z, e.g.. $z_1 = 10z$, and, after a certain number of approximations, to investigate whether it holds $n_i \geqq z_1$ for $i = 1, 2, ..., N$. If, for some i, it holds $n_i < z_1$, the ith component will be neglected in the following calculation and its concentration will be set equal to zero, i.e., $n_i = 0$. Since 10^{-c} is always greater than z, the neglect of components for which it holds $n_i < z_1 < 10^{-c}$ has no effect on the calculation.

At the beginning of the calculation, i.e., during the choice of the first approximation, it can be assumed that the system contains as its components all possible elements either in an atomic or a molecular form. Components, the mass amounts of which in the mixture will drop below z_1, can be then eliminated during the calculation. It is suitable to arrange the elements and components in the constitutional matrix in accordance with the following order:

	P_1	P_2	$\cdots$	P_{M-1}	P_M
S_1	a_{11}	0	$\cdots$	0	0
S_2	0	a_{22}	$\cdots$	0	0
.	.	.	$\cdots$	.	.
.	.	.	$\cdots$	.	.
.	.	.	$\cdots$	.	.
S_{M-1}	0	0	$\cdots$	$a_{M-1,M-1}$	0
S_M	0	0	$\cdots$	0	a_{MM}
S_{M+1}	$a_{M+1,1}$	$a_{M+1,2}$	$\cdots$	$a_{M+1,M-1}$	$a_{M+1,M}$
.	.	.	$\cdots$	.	.
.	.	.	$\cdots$	.	.
S_N	a_{N1}	a_{N2}	$\cdots$	$a_{N,M-1}$	a_{NM}

As long as the original mixture contains ions and electrons, it holds $P_M = \dot{S}_M = e^-$, $a_{MM} = 1$, $b_M = 0$. For the elements of the constitutional matrix it holds:

for $i = 1, 2, ..., M$:

$$a_{ii} > 0 , \quad a_{ij} = 0 \quad \text{for} \quad i \neq j$$

for $i = M + 1, M + 2, ..., N$:

$$a_{ij} \geqq 0 \quad \text{for} \quad j = 1, 2, ..., M - 1$$

$$a_{iM} \geqq 0 \quad \text{for} \quad P_M \neq e^- .$$

The first approximation satisfies the balance conditions (3) and can be determined from $M + 1$ numbers, $n_1^{(1)}, n_2^{(1)}, ..., n_M^{(1)}, h$, so that it holds $n_{M+1}^{(1)} = n_{M+2}^{(1)} = ... = n_N^{(1)} = h$. The balance conditions (3) can be rearranged in the following manner as far as the assumptions about the constitutional matrix and the first approximation are satisfied

TABLE I

Temperature Dependence of the Equilibrium Composition of Dissociation and Ionization Products of SF_6 (in mole fractions)

Product	Temperature, K						
	1 000	1 500	2 000	2 500	3 500	4 000	5 000
S	0	7·4952−14	5·2127−07	1·3284−02	1·1690−01	1·3707−01	1·4228−01
F	9·1825−07[a]	1·6780−02	5·9579−01	9·0450−01	8·6801−01	8·5944−01	8·5725−01
e⁻	0	0	5·4975−19	3·9873−13	2·7769−08	7·0839−07	4·4123−05
S⁺	0	0	4·7084−13	4·6604−09	1·2096−06	5·6052−06	6·5674−05
S²⁺	0	0	0	0	0	0	0
S⁻	0	0	0	8·0589−13	9·7228−09	7·8997−08	7·4603−07
F⁻	0	0	4·7077−13	4·6592−09	1·1721−06	4·8178−06	2·0806−05
F⁺	0	0	0	0	0	1·5199−13	9·8926−11
S₂	0	1·7651−18	1·6512−08	6·2052−02	1·3073−02	2·8194−03	2·2561−04
F₂	9·1014−11	3·9166−05	1·7100−03	5·1853−04	4·6992−05	2·2398−05	7·5920−06
SF₆	9·9998−01	9·7473−01	1·0294−01	1·8101−06	2·6483−17	0	0
SF₄	1·4282−05	8·4473−03	2·9952−01	5·2074−03	5·2777−10	2·0845−12	6·8768−16
SF₂	2·7404−17	3·7613−10	2·7562−05	1·4056−03	3·4242−06	3·0578−07	8·0345−09
SF	0	1·3820−11	1·0915−05	1·3034−02	1·9629−03	6·3530−04	1·0338−04

[a] $9·1825−07 = 9·1825 \cdot 10^{-7}$.

$$a_{jj}n_j^{(1)} + \sum_{k=M+1}^{N} a_{kj}h = b_j, \quad j = 1, 2, \ldots, M$$

$$a_{jj}n_j^{(1)} + hs_j = b_j; \quad s_j = \sum_{k=M+1}^{N} a_{kj}$$

$$n_j^{(1)} = [b_j - hs_j]/a_{jj}. \tag{4}$$

Since $a_{jj} > 0$, the requirement of $n_j^{(1)} > 0$ leads to

$$b_j - hs_j > 0,$$

$$hs_j < b_j.$$

If $P_M \neq e^-$, it holds $s_j \geqq 0$ and the last inequality passes to

$$h < b_j/s_j$$

TABLE I
(Continued)

Product	Temperature, K						
	6 000	7 000	8 000	10 000	12 000	15 000	20 000
S	1·4217−01	1·3989−01	1·3289−01	9·2093−02	3·4823−02	5·9955−03	6·5778−04
F	8·5672−01	8·5495−01	8·4966−01	8·1860−01	7·6746−01	5·9475−01	9·7927−02
e⁻	4·8327−03	2·5210−03	8·6551−03	4·4602−02	9·8831−02	1·9971−01	4·5530−01
S⁺	5·2052−04	2·5693−03	8·7136−03	4·4387−02	9·3912−02	1·0813−01	6·7966−02
S²⁺	8·2700−17	7·3342−14	1·2660−11	1·8323−08	2·3872−06	1·9978−04	9·1902−03
S⁻	2·0644−06	3·7146−06	6·1008−06	5·2685−06	1·7003−06	1·9501−07	1·0717−08
F⁻	3·5195−05	4·4960−05	5·8893−05	4·7629−05	2·9553−05	1·2280−05	1·0137−06
F⁺	1·1570−03	3·8632−07	6·5177−06	2·6786−04	4·9457−03	9·1195−02	3·6896−01
S₂	3·9713−05	1·5370−05	4·0204−06	0	0	0	0
F₂	3·6399−06	2·0866−06	1·2909−06	0	0	0	0
SF₆	0	0	0	0	0	0	0
SF₄	3·1669−18	0	0	0	0	0	0
SF₂	6·6801−10	8·1182−11	1·6574−11	0	0	0	0
SF	2·9156−05	9·9643−06	4·2991−06	0	0	0	0

in which $b_j/s_j = +\infty$ for $s_j = 0$. Let

$$m_0 = \min\left(b_j/s_j\right), \quad j = 1, 2, \ldots, M.$$

An arbitrary number from the range $(0, m_0)$ can be substituted for h and the numbers $n_1^{(1)}, n_2^{(1)}, \ldots, n_M^{(1)}$ are determined from relation (4). If $P_M = e^-$, it holds $s_j \geqq 0$ for $j = 1, 2, \ldots, M - 1$ and the three following cases must be distinguished:

$1)$ $s_M < 0$: let $m_1 = \min\left(b_j/s_j\right)$; for $s_j = 0$ it holds $b_j/s_j = +\infty$ $(j = 1, 2, \ldots, M - 1)$ An arbitrary number from the range $(0, m_1)$ can be substituted for h and the numbers $n_1^{(1)}, n_2^{(1)}, \ldots, n_M^{(1)}$ are determined from relation (4).

$2)$ $s_M = 0$: h is an arbitrary number from the range $(0, m_1)$, the numbers $n_1^{(1)}, n_2^{(1)}, \ldots, n_{M-1}^{(1)}$ are determined from relation (4) and $n_M^{(1)} = z_1$.

$3)$ $s_M > 0$: $h = z_1$, $n_j^{(1)} = b_j/a_{jj}$ for $j = 1, 2, \ldots, M - 1$, $n_M^{(1)} = z_1$.

The last case is universal to the extent that it can be used for calculating the first approximation in all instances. If $P_M \neq e^-$, then $n_M^{(1)} = b_M/a_{MM}$.

A similar procedure can be derived for calculating the first approximation on the assumption that it is determined by numbers $n_1^{(1)}, n_2^{(1)}, \ldots, n_M^{(1)}, h$ and that value of the ratio $n_{M+1}^{(1)} : n_{M+2}^{(2)} : \ldots : n_N^{(1)}$ is prescribed.

TABLE II

Dependence of the Equilibrium Composition of Dissociation and Ionization Products of SF_6 on the Total Pressure at 3 000 K   (in mole fractions)

Product	Pressure, MPa						
	0·1	0·2	0·4	0·8	1·0	1·5	2·0
S	6·0790—02	4·6196—02	3·4141—02	2·4596—02	2·1989—02	1·7689—02	1·4845—02
F	8·9179—01	8·9670—01	8·9945—01	8·9896—01	8·9749—01	8·9075—01	8·7913—01
e^-	2·9263—10	1·2730—10	5·4661—11	2·3211—11	1·7573—11	1·0548—11	7·2957—12
S^+	1·3510—07	1·1800—07	1·0155—07	8·6147—08	8·1381—08	7·2709—08	6·6168—08
S^{2+}	0	0	0	0	0	0	0
S^-	2·8402—10	1·8779—10	1·1918—10	7·2922—11	6·1696—11	4·4687—11	3·4585—11
F^-	1·3453—07	1·1769—07	1·0138—07	8·6050—08	8·1301—08	7·2653—08	6·6126—08
F^+	0	0	0	0	0	0	0
S_2	4·1562—02	4·8003—02	5·2437—02	5·4432—02	5·4381—02	5·2787—02	4·9571—02
F_2	1·3023—04	2·6333—03	5·2990—04	1·0586—03	1·3190—03	1·9488—03	2·5211—03
SF_6	1·1623—12	5·8466—11	2·8164—09	1·2943—07	4·3707—07	3·8278—06	1·6682—05
SF_4	5·7813—07	7·1855—06	7·6008—05	9·8922—04	2·1450—03	8·4758—03	2·1331—02
SF_2	5·5686—05	1·7114—04	5·0901—04	1·4652—03	2·0400—03	3·6372—03	5·2858—72
SF	5·6684—03	8·6626—03	1·2843—02	1·8495—02	2·0635—02	2·4712—02	2·7291—02

In this work we used the WJD method with our procedure for finding the first approximation to calculate the composition of dissociation and ionization products of sulphur hexafluoride on the assumption of the ideal behaviour at temperatures of $1\,000-20\,000$ K and pressures of $0\cdot1-2\cdot0$ MPa. The calculation was performed on a Minsk-22 computer with $c = 8$, $z = 5\cdot421 . 10^{-20}$, $z_1 = 10^{-18}$. The temperature dependence of the equilibrium composition of dissociation and ionization products of SF_6 is given in Table I; Table II contains the pressure dependence of the composition at 3000 K.

Except for F^+, the results of our calculations agree well with those published by Belov[10], who employed in this calculations Kandiner's method[1], which is based on equilibrium constants. We could not compare our results with other authors, because they report their results only graphically. The thermodynamic functions in our calculation were taken from tables[11] and from Belov's work[10]. We also employed successfully the method outlined for calculating the composition of equilibrium mixtures of SF_6 with N_2, H_2O and air at different ratios.

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