CALCULATION OF THE EQUILIBRIUM COMPOSITION OF REACTING GAS SYSTEMS

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The method of [1] for calculating the composition is considered, but with allowance for the selection of the "optimum" basis.

The chemical reactions in a system of n components and k elements can be written in the form

$$R_i-\sum_{j=1}^{k}A_{ij}R_j=0,\quad i=k+1,\ \ldots,\ n.\tag{1}$$

Then the system of equations for the determination of the equilibrium composition of the mixture of n components, including ionized components, and k elements (together with the electron) consists of k equations of balance of the elements (one of them is the equation of conservation of charge), the normalization condition (the Dalton law), and (n—k) equations of the law of mass action for the (n—k) independent reactions of (1). From this system one determines the number of moles of the components N_i (i = 1, 2, ..., n) and the total number of moles of the system N:

$$\sum_{i=1}^{n}N_i-N=0,\tag{2}$$

$$\sum_{i=1}^{n}A_{ij}N_i-\sum_{i=1}^{n}A_{ij}N_i^0=0,\tag{3}$$

$$\ln N_i=\ln K_{pi}+\Big(\sum_{j=1}^{k}A_{ij}-1\Big)\ln p+\Big(1-\sum_{j=1}^{k}A_{ij}\Big)\ln N+\sum_{j=1}^{k}A_{ij}\ln N_j,\tag{4}$$

where j = 1, 2, ..., k; i = k + 1, ..., n.

The nonlinear system of equations (2)-(4) is solved by Newton's method [1]. The linear system of equations (5), (6), which is solved by the method of iterations together with (4), is obtained relative to the corrections $\Delta\ln N$ and $\Delta\ln N_j$:

$$\sum_{j=1}^{k}\Delta\ln N_j\sum_{i=1}^{n}A_{ij}N_i+\Delta\ln N\Big[\sum_{i=1}^{n}\Big(1-\sum_{j=1}^{k}A_{ij}\Big)N_i-N\Big]+\sum_{i=1}^{n}N_i-N=0,\tag{5}$$

$$\sum_{j=1}^{k}\Delta\ln N_j\sum_{i=1}^{n}A_{il}A_{ij}N_i+\Delta\ln N\sum_{i=1}^{n}A_{il}\Big(1-\sum_{j=1}^{k}A_{ij}\Big)N_i$$

$$+\sum_{i=1}^{n}A_{il}N_i-\sum_{i=1}^{n}A_{il}N_i^0=0,\ l=1,\ 2,\ \ldots,\ k.\tag{6}$$

The convergence of the method is improved if the components which predominate in a specific region of the p—T diagram are chosen as the basis components [1].

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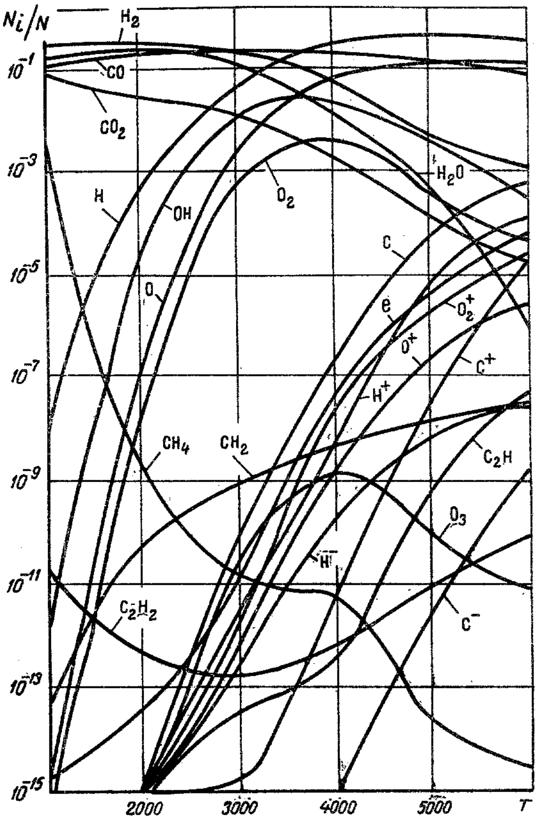

Fig. 1. Variation in concentrations of components N_i/N of system formed by the mixture $0.35\ CO_2 + 0.65\ H_2$ as a function of temperature T (°K). p = 1 atm; T, °K.

If each component of system (1) is represented in the form of a vector in a k-dimensional linear space then the transition from one set of predominant components (the basis) to another is accomplished according to the rules of linear transformation of coordinates. The transition matrix $\|B^{-1}\|$ consists of the coefficients of resolution of the vectors of the old basis with respect to the new. The coordinates of a vector relative to the new basis are expressed linearly through the coordinates of the vector relative to the old basis:

$$\|A_{ij}^{(n)}\| = \|B^{-1}\|^* \|A_{ij}\|. \tag{7}$$

The form of Eqs. (2)-(4) is retained in the transition to the new basis. In this case each time it becomes necessary to convert to a new basis one must recalculate the matrix of stoichiometric coefficients $\|A_{ij}\|$ and the equilibrium constant K_{pi} of the reactions under consideration. In [1] the values K_{pi} were calculated from the equation

$$K_{pi} = \exp\left\{-\left[H_i - TS_i - \sum_{j=1}^{k} A_{ij}(H_j - TS_j)\right]/RT\right\}. \tag{8}$$

This equation provides for the calculation of the equilibrium constants K_{pi} in any basis. Often, however, for some components the values of the enthalpy and entropy are not known for all the range of p and T studied, but the K_{pi} are known for all the reactions in the form of tables or approximations [2]. In such cases Eq. (8) cannot be used, and the recalculation of the equilibrium constants of the system of reactions (1) in the transition to the new basis can be conducted according to the equations

$$\ln K_{pi}^{(n)} = \ln K_{pi} - \sum_{j=1}^{k} A_{ij}^{(n)} \ln K_{pj}, \quad i = k+1, \ldots, n. \tag{9}$$

After the calculation of the composition one can compute the thermodynamic characteristics of the mixture:

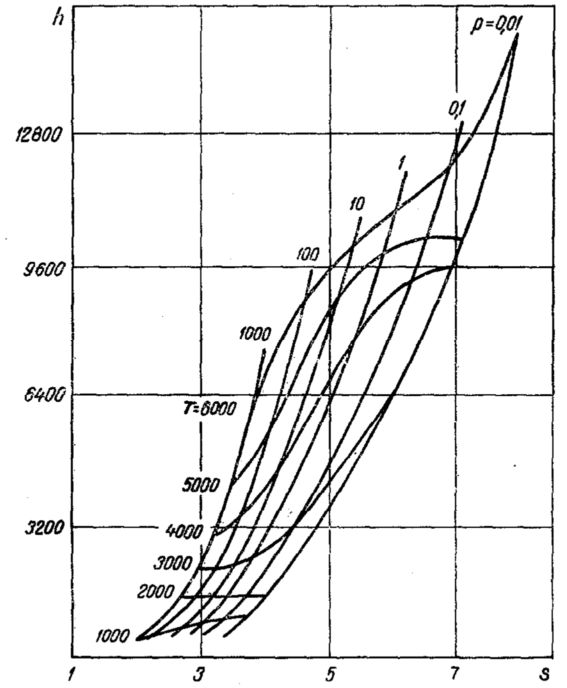

Fig. 2. h(cal/g)-s (cal/g•deg) diagram of system formed by the mixture 0.35 CO_2 + 0.65 H_2.

$$\mu = \mu_0 \frac{N^0}{N}, \quad h = \frac{1}{\mu} \sum_{i=1}^{n} H_i \frac{N_i}{N}, \quad u = h - \frac{RT}{\mu}, \tag{10}$$

$$s = \frac{1}{\mu} \left[\sum_{i=1}^{n} S_i \frac{N_i}{N} - R \ln p - R \sum_{i=1}^{n} \frac{N_i}{N} \ln \frac{N_i}{N} \right], \tag{11}$$

$$c_p = \frac{1}{\mu_0 N_0} \left[\sum_{i=1}^{n} C_{pi} N_i + \sum_{i=1}^{n} H_i \frac{1}{T} N_i \left(\frac{\partial \ln N_i}{\partial \ln T} \right)_p \right], \tag{12}$$

$$c_v = c_p + \frac{R}{\mu_0 N_0} \frac{\left[1 + \left(\frac{\partial \ln N}{\partial \ln T} \right)_p \right]^2}{\left[\left(\frac{\partial \ln N}{\partial \ln p} \right)_T - 1 \right]}, \quad a^2 = \frac{\gamma R T}{\mu} \frac{1}{1 - \left(\frac{\partial \ln N}{\partial \ln p} \right)_T}. \tag{13}$$

In this case the values of the derivatives $(\partial \ln N/\partial \ln T)_p$, $(\partial \ln N_i/\partial \ln T)_p$, $(\partial \ln N/\partial \ln p)_T$, $(\partial \ln N_i/\partial \ln p)_T$ needed for the calculation of c_p, c_v, and a^2 is found by solving a system of equations whose determinant coincides with the determinant of system (5)-(6) in the last cycle of iterations [1].

For each value of p, T one must choose the basis in such a way that the method of successive approximations used to calculate the composition converges. In order for system (4)-(6) to have a well specified matrix it is necessary that $N_i/N_j \ll 1$, $j = 1, 2, \ldots, k$; $i = k + 1, \ldots, n$. From (4) it follows that for this it is desirable that $\ln K_{pi} \leq 0$ $(i = k + 1, \ldots, n)$.

Let us write Eq. (4) in the form

$$\ln p_i - \sum_{j=m+1}^{n} A_{ij} (\ln p_j) = \ln K_{pi}, \quad i = 1, 2, \ldots, m = n - k. \tag{14}$$

We will consider the columns of the matrix of system (14) to be vectors $\mathbf{P}_i$ of a space of dimenality $m = n - k$. The first m unit vectors correspond to the "nonpredominant" components and they can be chosen as the basis in this space, and then the last k vectors, corresponding to the "predominant" components in this basis, have the coordinates $(-A_{ij})$. Thus, the basis consists of $\mathbf{P}_1$, $\mathbf{P}_2 \ldots$, $\mathbf{P}_m$, where $\mathbf{P}_i = (0, \ldots, 0, 1, 0, \ldots, 0)$; the nonbasis vectors are $\mathbf{P}_j = (-A_{1j}, \ldots, -A_{mj})$, and the vector of the right

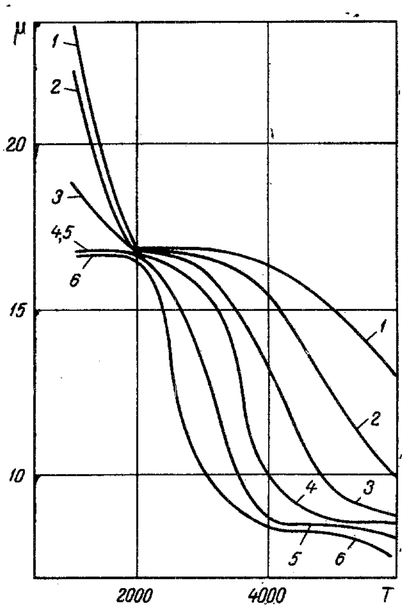

Fig. 3. Variation in a molecular weight μ (g/mole) of the system formed by $0.35\ CO_2 + 0.65\ H_2$ as a function of temperature: 1) p = 1000 atm; 2) 100; 3) 10; 4) 1; 5) 0.1; 6) 0.01. T, °K.

sides of the system is $P_0 = (\ln K_{p1}, \ldots, \ln K_{pm})$. Let us expand the vectors P_j and P_0 with respect to the basis vectors P_i:

$$\mathbf{P}_0 = (\ln K_{p1})\,\mathbf{P}_1 + \ldots + (\ln K_{pi})\,\mathbf{P}_i + \ldots + (\ln K_{pm})\,\mathbf{P}_m, \tag{15}$$

$$\begin{aligned}\mathbf{P}_j &= (-A_{1j})\,\mathbf{P}_1 + \ldots + (-A_{ij})\,\mathbf{P}_i + \ldots + (-A_{mj})\,\mathbf{P}_m = \\ &= \varphi_{1j}\mathbf{P}_1 + \ldots + \varphi_{ij}\mathbf{P}_i + \ldots + \varphi_{mj}\mathbf{P}_m.\end{aligned} \tag{16}$$

We multiply P_j by some number θ and subtract from P_0:

$$\begin{aligned}\mathbf{P}_0 = \theta\mathbf{P}_j &+ (\ln K_{p1} - \theta\varphi_{1j})\,\mathbf{P}_1 + \ldots + (\ln K_{pi} - \theta\varphi_{ij})\,\mathbf{P}_i + \ldots \\ &+ (\ln K_{pm} - \theta\varphi_{mj})\,\mathbf{P}_m.\end{aligned} \tag{17}$$

The vector P_0 is expanded in (17) with respect to (m + 1) vectors. Since the basis consists of m vectors, θ must be selected in such a way that the coefficient on one of the P_i will equal zero. Then P_0 will be expanded with respect to a new basis in which P_j will be included and one of the P_i excluded. It is desirable to choose the new basis so that the expansion coefficients of P_0 ($\ln K_{pi}$) will be negative. In order that one of the coefficients on P_i will equal zero it is necessary to choose (i, j are not yet fixed)

$$\theta_{ij} = \frac{\ln K_{pi}}{\varphi_{ij}}, \quad \varphi_{ij} \neq 0, \quad i = 1,\ 2,\ \ldots,\ m, \quad j = m+1,\ \ldots,\ n. \tag{18}$$

Then the coefficients of P_0 in the new basis $P_1, \ldots, P_{i-1}, P_{i+1}, \ldots, P_m, P_j$ are:

$$\begin{aligned}\ln K_{pr}^{(n)} &= \ln K_{pr} - \frac{\ln K_{pi}}{\varphi_{ij}}\,\varphi_{rj}, \quad r \neq i, \ r = 1,\ 2,\ \ldots,\ m, \\ \ln K_{pi}^{(n)} &= \frac{\ln K_{pi}}{\varphi_{ij}}, \quad j = m+1,\ \ldots,\ n.\end{aligned} \tag{19}$$

Let us find the indices i1, j1 such that $F_{i1,j1} \le F_{ij}$, where $F_{ij} = \max\limits_{(r \neq i)} [\ln K_{pr} - (K_{pi}/\varphi_{ij})\,\varphi_{rj}]$, i.e., $F_{i1,j1}$ equals

$$F_{i1,\,j1} = \min_{(i,\,j)} \{F_{ij}\} = \min_{(i,\,j)} \left\{ \max_{(r \neq i)} \left(\ln K_{pr} - \frac{\ln K_{pi}}{\varphi_{ij}}\,\varphi_{rj} \right) \right\} \tag{20}$$

for $\ln K_{pi}/\varphi_{ij} < 0$, i = 1, 2, ..., m, j = m + 1, ..., n. Then

$$\theta_{i1,\,j1} = \frac{\ln K_{pi1}}{\varphi_{i1,\,j1}}, \tag{21}$$

while the vector $P_0 = \sum\limits_{i=1}^{m} \ln K_{pi}^{(n)}\ P_i$ in the new basis will have the coordinates

$$\begin{aligned}\ln K_{pi}^{(n)} &= \ln K_{pi} - \frac{\ln K_{pi1}}{\varphi_{i1,\,j1}}\,\varphi_{i,j1}, \quad i \neq i1, \\ \ln K_{pi1}^{(n)} &= \frac{\ln K_{pi1}}{\varphi_{i1,\,j1}}.\end{aligned} \tag{22}$$

The nonbasis vectors P_j in the new basis will have the coordinates

$$\begin{aligned}\varphi_{ij}^{(n)} &= \varphi_{ij} - \frac{\varphi_{i1,\,j}}{\varphi_{i1,j1}}\,\varphi_{i,\,j1}, \quad i \neq i1, \\ \varphi_{i1,j}^{(n)} &= \frac{\varphi_{i1,\,j}}{\varphi_{i1\ j1}}.\end{aligned} \tag{23}$$

It is seen that Eqs. (22) and (23) represent one step in the Gauss–Jordan elimination method but with a special choice of the leading element in accordance with (20).

There will be zeros everywhere in column j1 except for row i1 in which there will be a 1, while column i1 becomes different from unity. In general, if the desired basis is known beforehand then the matrix $\|D\|$ is constructed from the columns of the initial matrix corresponding to the vectors of the new basis and then the initial matrix is multiplied by $\|D^{-1}\|$. Then

$$P_i^{(n)} = \|D^{-1}\| P_i, \quad P_0^{(n)} = \|D^{-1}\| P_0 \tag{24}$$

and the new matrix $\|P_1, \ldots, P_i, \ldots, P_m, P_0\|$ is obtained, but already in the new basis. At the same time the components of $P_0^{(n)}$ are $\ln K_{pi}^{(n)}$ in the new basis. However, since it is not known beforehand what basis must be chosen, it is necessary to change from basis to basis by the method presented above, changing one vector at each step. Let us lay out this method by steps.

1. The initial basis is chosen.
2. If all the $\ln K_{pi} < 0$ in this basis then the basis is chosen and the process is ended.
3. If there are $\ln K_{pi} > 0$ then for all i, j, $\varphi_{ij} \neq 0$ one chooses $\ln K_{pi}/\varphi_{ij} < 0$.
4. One finds

$$\max_{(r \neq i)} \left(\ln K_{pr} - \frac{\ln K_{pi}}{\varphi_{ij}} \varphi_{rj} \right) = F_{ij}.$$

5. One determines the i1, j1 such that $F_{i1,j1} = \min_{i,j} F_{ij}$.

6. A vector P_{i1} is eliminated and P_{j1} is included in the basis. For this the new coefficients $\varphi_{ij}^{(n)}$ of the system are computed from (23) and the $\ln K_{pi}^{(n)}$ from (22). Then the process is repeated from step 2.

If $\ln K_{pi}/\varphi_{ij} \geq 0$ for all i, j in step 3 then the process can be continued further, but in the new basis $K_{pi}^{(n)} \geq 0$, and only after several steps can one obtain $\ln K_{pi1}^{(n)} < 0$. It is seen that the process described above is the minimization of some nonlinear function of the type

$$F = \min_{\text{(by bases)}} \varphi \{ \max_{(i)} \ln K_{pi} \}. \tag{25}$$

Since the function (25) is nonlinear it is impossible to predict in advance whether the process will give an absolute minimum. However, for a solution one does not need an absolute minimum but only a small enough value of F. The meaning of the algorithm presented is that in each step one seeks a basis in which one of the values $\ln K_{pi1} > 0$ is decreased and at the same time the remaining values $\ln K_{pr}$ ($r \neq i1$), if they increase, must increase in a minimal way. As a rule, after a few steps one is able to obtain $\ln K_{pi} < 0$, since one can guess rather close to the desired basis as a function of p, T.

For the majority of systems of equilibrium chemical reactions (1) considered in practice one can find a basis in which $\ln K_{pi} \leq 0$. For this it is necessary that

$$K_{pi} = \frac{p_i}{\prod_{j=1}^{k} p_j^{A_{ij}}} \leqslant 1, \quad p_i \leqslant \prod_{j=1}^{k} p_j^{A_{ij}}. \tag{26}$$

It is clear, however, that (26) must not be satisfied for every system of type (14). Therefore the method must be changed as follows. From the set of n vectors in the k-dimensional vector space one can construct a finite number of basis sets $N \leq C_n^k$.

It is clear that among these N sets one can choose one (we will call it the optimum set) in which Eq. (25) is satisfied. The method given above is also suitable for this general case without changes, but now the minimum value of $\ln K_{pi}$ by bases can be obtained as positive.

On the basis of the method described a standard program was compiled for the calculation of the composition and thermodynamic functions on a Minsk-22 computer, and a calculation was carried out for a composite of CO_2 and H_2 containing the following 26 components: H, O, C, e, CO_2, CO, CH_2, CH_4, C_2H, C_2H_2, C_2H_4, H_2, O_2, O_3H^+, H^-, $O^{\pm}$, O^-, C^+, C^-, O_2^+, OH^+, OH^-, H_2O, OH, CO^+. Since at present there are no data in the literature on the composition of systems formed of CO_2 and H_2 taken in different quantitative ratios to each other the data obtained can be useful in the study of phenomena taking place in a plasma stabilized by a mixture of CO_2 and H_2.

The calculation was conducted for temperatures from 1000 to 6000°K and pressures from 0.01 to 1000 atm. The following were calculated: the composition N_i (in moles), the specific enthalpy h (cal/g), the internal energy u (cal/g), the entropy s (cal/g · deg), the molecular weight μ (g/mole).

The composition of the system formed by a mixture of $0.35\ CO_2 + 0.65\ H_2$ as a function of the temperature for $p = 1$ atm is presented in Fig. 1.

The h—s diagram of this system is shown in Fig. 2.

The dependence of the molecular weight of the system on the temperature for pressures from 0.01 to 1000 atm is given in Fig. 3.

NOTATION

R_i: component i; N_i, H_i, S_i, C_{pi}, p_i: number of moles, enthalpy, entropy, and heat capacity of component i and partial pressure; N_j, H_j, S_j: number of moles, enthalpy, and entropy of basis (predominant) component j; N, N_0: total number of moles of system at p, T and in initial state; N_i^0: initial number of moles of component i in standard state; p: pressure; T: temperature; K_{pi}, $K_{pi}^{(n)}$: equilibrium constant of reaction i in old and new basis; A_{ij}, $A_{ij}^{(n)}$: matrix element of stoichiometric coefficients in old and new bases; $\|B^{-1}\|$: matrix of transition from old to new basis in k-dimensional linear space; $\|D^{-1}\|$: transition matrix in m-dimensional space; h, u, s, c_p, c_v, a: specific enthalpy, internal energy, entropy, heat capacity at p = const, heat capacity at v = const, and speed of sound in system; μ, μ_0: molecular weight at p, T and in initial state; γ: ratio of heat capacities c_p/c_v; R: gas constant.

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