distribution in the conductor (7). Dimensional quantities: α, temperature resistance coefficient; σ_0, initial electrical conductivity of the conductor at infinity; χ, thermal conductivity; γ, density; c, heat capacity; R characteristic inhomogeneity dimension; J_0, amplitude of the current density.

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THERMODYNAMIC EQUILIBRIUM OF A GAS MIXTURE WITH A SOLUTION IN THE CONDENSED PHASE

A. V. Kamennykh and G. P. Yasnikov

UDC 541.123

A thermodynamic analysis is made of the equilibrium of a gas mixture (using a nitrogen–hydrogen mixture as an example) with a solid solution of its components. The processes occurring in the surface layer and interphase exchange are taken into account. The equilibrium characteristics are determined in terms of the equilibrium constants of the intermediate stages of the surface reactions.

The penetration of a gas into a condensed material and the dissolution of gas-mixture components in the solid phase is a complex process consisting of a series of elementary stages: adsorption, desorption, dissociation, and recombination. The kinetics of such a process, the concentration of the dissolved gases, and other characteristics of the interaction of the gas with the solid depend on the rates of the surface reactions and the elementary stages [1]. Under certain conditions these stages can have a decisive effect on the process rate. Traditional methods of describing equilibrium solubility based on directly equating the chemical potentials of the dissolved atoms in the various phases and on the surface are often inapplicable. This is because, e.g., atoms can appear on the surface as a result of dissociation, catalyzed by the solid phase, and may be absent in the gas phase, which contains only molecular gas. Below we make a thermodynamic analysis of such a system with allowance for the dissolution of the gas-mixture components, which is of interest for the chemical and thermal treatment of materials.

Specifically, we consider a nitrogen–hydrogen mixture that contains nitrogen, hydrogen, and ammonia and interacts with solutions of the components in the solid phase, taking into account the effect of the surface of the solid catalyst. This thermodynamic system contains two bulk phases (gas and solid) and one surface phase. We note that heterogeneous processes

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A. M. Gorkii Ural State University. S. M. Kirov Ural Polytechnical Institute, Ekaterinburg. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 62, No. 4, pp. 624-628, April, 1992. Original article submitted July 30, 1991.

1062-0125/92/6204-0460$12.50

are characterized by a substantial delimitation of the homogeneous media and the surface separating them [2] and so the surface layer must be distinguished.

We assume that the gas phase contains molecular nitrogen, hydrogen, and ammonia, which do not dissociate into atoms and radicals but perhaps react according to the scheme $3/2H_2 + 1/2N_2 \rightleftarrows NH_3$ with equilibrium constant K. The partial gas pressure is denoted by p_i (here $i = 1, 2, 3$ for hydrogen, nitrogen, and ammonia, respectively). Molecules are adsorbed on the surface of the solid catalyst and are desorbed into the gas phase.

In the adsorbed state on the surface [3] molecules and radicals dissociate into atoms and radicals and the reverse recombination occurs in the reactions

$$\begin{gathered} H_2 \rightleftarrows 2H,\ N_2 \rightleftarrows 2N,\ NH_3 \rightleftarrows H + NH_2, \\ NH_2 \rightleftarrows H + NH,\ NH \rightleftarrows H + N; \end{gathered} \tag{1}$$

other reactions can also be considered, e.g.,

$$\begin{gathered} NH_3 \rightleftarrows NH + 2H,\ NH_3 \rightleftarrows N + 3H, \\ NH_2 \rightleftarrows N + 2H,\ 2NH_3 \rightleftarrows N_2 + 3H_2. \end{gathered} \tag{2}$$

If x_1, x_2, and x_3 are the relative fractions of the surface layer occupied by H_2, N_2, and NH_3 molecules and y_1, y_2, y_3 and y_4 are the relative fractions of the surface occupied by H, N atoms and NH_2 and NH radicals, respectively, we find the unoccupied fraction of the surface to be

$$\varphi = 1 - \sum_{i=1}^{3} x_i - \sum_{j=1}^{4} y_j. \tag{3}$$

We assume that hydrogen and nitrogen atoms appear and only one they can dissolve in the condensed phase and emerge from it into the surface layer (i.e., are desorbed and are adsorbed by the solid phase). For simplicity we assume that no reactions with the participation of hydrogen and nitrogen atoms occur in the solution. We introduce the relative concentrations ω_j for solutions of atoms in the catalyst bulk, i.e., the ratios of the numerical volume concentrations to the concentration of all the accessible interstices c_* ($j = 1, 2$ pertain to hydrogen and nitrogen atoms, respectively). The fraction of unoccupied sites in the bulk of the condensed phase ψ is

$$\psi = 1 - \sigma_1 - \sigma_2,\quad \sigma_j = \omega_j|_{n=0},\quad j = 1, 2, \tag{4}$$

where n is the coordinate measured along the normal to the surface (n = 0) in the reaction of the gas phase.

To determine the number of linearly independent basic reactions from the set of all possible reactions (1), (2), we consider the balance of the number of subcomponents that participate in the transformations, using the method of [4]. Hydrogen (s = 1) and nitrogen (s = 2) atoms, which do not change their chemical properties during the transformation, act as subcomponents S_s. The chemical compounds participating in the reactions (including N and H) are components S_k ($k \neq s$). For the series H_2, N_2, NH_3, N, H, NH_2, and NH we have k = 1, ..., 7, respectively. Two subcomponents and seven components thus exist in the system.

The total number of atoms of each subcomponent remains constant during all the chemical transformations:

$$\sum_{k=1}^{7} a_{sk} \Delta S_k = 0,\quad s = 1, 2,\quad k = 1, \ldots, 7. \tag{5}$$

Here ΔS_k is the change in the number of particles of component k; the elements of the matrix

$$\|a_{sk}\| = \begin{Vmatrix} 0 & 2 & 1 & 0 & 1 & 1 & 1 \\ 2 & 0 & 3 & 1 & 0 & 2 & 1 \end{Vmatrix}$$

represent the number of atoms of the subcomponents (nitrogen and hydrogen) that appear in the molecules of the components of the series under consideration; the rank of the matrix is $\mathrm{Rg}\|a_{sk}\| = 2$.

The system of two homogeneous equations with seven unknowns has $R = K - \mathrm{Rg}\|a_{sk}\| = 7 - 2 = 5$ linearly independent solutions that form a normal fundamental system. Thus, $R = 5$ linearly independent reactions occur in the system.

Writing the solution of the fundamental system as a column vector $\Delta S_1, \ldots, \Delta S_5$, we form the matrix $\|\Delta S_{kr}\|$, $k = 1, \ldots, 7$, $r = 1, \ldots, 5$, $\mathrm{Rg}\|\Delta S_{kr}\| = 5$ since all the columns are linearly independent. The linear combinatiok of solutions ΔS_r can be used to construct a different system of solutions, $\Delta S_i = \sum\limits_{r=1}^{5} \Delta S_r C_r$, where C_r are arbitrary factors. If the degrees of completeness $\xi_r (C_r \equiv \xi_r)$ of the reactions are assumed to be C_r, then on dividing each term of the last equation for ΔS_i by the Avogadro number N_A we obtain the balance of the number of moles of component k in the chemical transformations: $\Delta n_k = \sum \nu_{kr}\xi_r = \Delta S_k/N_A$. Since ΔS_i is a solution of (3), it follows from this system that

$$\sum_k a_{sk}\nu_{kr} = 0 \quad \text{or} \quad \begin{vmatrix} 0 & 2 & 1 & 0 & 1 & 1 & 1 \\ 2 & 0 & 3 & 1 & 0 & 2 & 1 \end{vmatrix} \times \begin{vmatrix} \nu_{11} \ldots \nu_{15} \\ \nu_{71} \ldots \nu_{75} \end{vmatrix} = 0. \tag{6}$$

The matrix equation (6) is satisfied by the stoichiometric coefficients of the surface reactions (reaction numbers r = 1, ..., 5, respectively, correspond to the reaction numbers in (1)): $\nu_{11} = \nu_{22} = \nu_{33} = \nu_{64} = \nu_{75} = -1$, $\nu_{41} = \nu_{52} = 2$, $\nu_{43} = \nu_{44} = \nu_{45} = \nu_{55} = \nu_{63} = \nu_{74} = 1$, all the other elements of the matrix $\|\nu_{kr}\|$ are zero. The conservation of mass during the transformations $\sum\limits_k \mu_k^0 \Delta n_k = \sum\limits_r \sum\limits_k \nu_{kr}\mu_k^0\xi_r = 0$ infers the stoichiometric equations of the reactions $\sum\limits_k \nu_{kr}\mu_k^0 = 0$. Since all the columns of $\|\nu_{kr}\|$ are linearly independent (rank $\mathrm{Rg}\|r_{kr}\| = 5$), the chemical reactions from (1) are also linearly independent, i.e., can be considered to be the basic reactions. All the other reactions from (2) can be obtained by a linear combination of the basic reactions.

By the Gibbs phase rule [5] the number of independent intensive parameters of the system is $W = 2 + (c - r) - \Phi$, where $c = 7$ is the number of components, $r = 5$ is the number of independent reactions, and $\Phi = 3$ is the number of phases in the system, i.e., $W = 1$; the pressure, temperature, or fraction of the surface layer occupied by some component can be used as such a parameter.

Next we consider the thermodynamic equilibrium conditions of the system, bearing in mind that the surface layer is a phase that contains seven components with chemical potentials μ_k.

The thermodynamic equilibrium conditions include:

– phase equilibrium, determined by the equality of the chemical potentials in the various phases $\mu_k = \mu_k^{(g)} = \mu_k^{(s)}$, $k = 1, \ldots, 7$, where the superscripts g and s denote gas and solid, respectively;

– chemical equilibrium $A_r = -\sum\limits_k \nu_{kr}\mu_k = 0$, $r = 1, \ldots, 5$.

Assuming that the gas mixture and solid solution are ideal, we write expressions for the chemical potentials [6]:

in the adsorbed layer for hydrogen, nitrogen, and ammonia molecules as well as atoms and radicals

$$\mu_k = \begin{cases} \mu_i = k_b T \ln(x_i/\varphi) + \mu_{0i}, & i = k = 1,\ 2,\ 3, \\ \mu_j = k_b T \ln(y_j/\varphi) + \mu_{0j}, & j = k - 3 = 1,\ 2,\ 3,\ 4; \end{cases} \tag{7}$$

in the gas phase for hydrogen, nitrogen, and ammonia molecules

$$\mu_i^{(g)} = k_b T \ln p_i + \mu_{0i}^{(g)}, \quad i = k = 1,\ 2,\ 3, \tag{8}$$

in the solid phase for hydrogen and nitrogen atoms

$$\mu_j = k_bT\ln(\sigma_j/\psi) + \mu_{0j}^{(S)}, \quad j = k - 3 = 1,2. \tag{9}$$

From the condition for equilibrium between the gas and the adsorbed layer we have $\mu_i = \mu_i^{(g)}$, whereupon for hydrogen, nitrogen, and ammonia molecules, respectively, we have

$$k_bT\ln(x_i/\varphi) = k_bT\ln p_i + (\mu_{0i}^{(g)} - \mu_{0i}), \quad x_i = a_ip_i\varphi, \quad i = k = 1,\ 2,\ 3,$$
$$a_i = \exp[(\mu_{0i}^{(g)} - \mu_{0i})/k_BT]. \tag{10}$$

The phase equilibrium between the adsorbed layer and the solid phase ($\mu_j = \mu_j^{(s)}$) enables us to obtain the surface concentrations for atomic solutions of hydrogen and nitrogen:

$$k_bT\ln(y_j/\varphi) = k_bT\ln(\sigma_j/\psi) + \mu_{0j}^{(S)} - \mu_{0j},$$
$$y_j/\varphi = b_j(\sigma_j/\psi), \quad b_j = \exp[(\mu_{0j}^{(S)} - \mu_{0j})/k_bT], \quad j = 1,2. \tag{11}$$

We consider the equilibrium condition for the basic reactions. To do this we use the expressions for the chemical potentials in terms of the reaction equilibrium constants $k_bT\ln K_r = -\sum_k \nu_{kr}\mu_{0k}$.

For the dissociation of hydrogen and nitrogen molecules (r = 1, 2)

$$k_bT\ln(x_i/\varphi) - 2k_bT\ln(y_i/\varphi) + \mu_{0i} - 2\mu_{0(i+3)} = 0,$$
$$y_i^2 = K_rx_i\varphi = a_iK_rp_i\varphi, \quad i = r = 1,\ 2.$$

For the dissociation of ammonia molecules (r = 3)

$$k_bT\ln(x_3/\varphi) - k_bT\ln(y_1/\varphi) - k_bT\ln(y_3/\varphi) - (\mu_{03} - \mu_{04} - \mu_{06}) = 0,$$
$$\ln(y_1/\varphi) + \ln(y_3/\varphi) - \ln(x_3/\varphi) = \ln K_3, \quad x_3\varphi = K_3y_1y_3.$$

For the dissociation of the ammonia radical (r = 4) we have

$$k_bT\ln(y_3/\varphi) - k_bT\ln(y_1/\varphi) - k_bT\ln(y_4/\varphi) - (\mu_{06} - \mu_{04} - \mu_{07}) = 0,$$
$$\ln(y_1/\varphi) + \ln(y_4/\varphi) - \ln(y_3/\varphi) = \ln K_4, \quad y_3\varphi = K_4y_1y_4.$$

For the dissociation of the ammonia radical (r = 5) we have

$$k_bT\ln(y_4/\varphi) - k_bT\ln(y_1/\varphi) - k_bT\ln(y_2/\varphi) - (\mu_{07} - \mu_{04} - \mu_{05}) = 0,$$
$$\ln(y_1/\varphi) + \ln(y_2/\varphi) - \ln(y_4/\varphi) = \ln K_5, \quad y_4\varphi = K_5y_1y_2.$$

Finally we have

$$x_i = a_ip_i\varphi, \quad i = 1,\ 2,\ 3, \quad y_j = \sqrt{d_ja_jp_j}\varphi, \quad j = 1,\ 2, \tag{12}$$

$$y_3 = d_3 a_3 p_3 \varphi / \sqrt{d_1 a_1 p_1},\ y_4 = d_4 d_3 a_3 p_3 \varphi / d_1 a_1 p_1,$$

where we have introduced the kinetic coefficient d_r ($d_r = K_r$) to make Eqs. (12) consistent with the relations obtained from an analysis of the kinetic model. From the last equation of (10), which was not used to derive (11), we obtain

$$K = \frac{d_5 d_4 d_3 a_3}{(d_1 a_1)^{3/2} (d_2 a_2)^{1/2}} = \frac{p_3}{p_1^{3/2}\ p_2^{1/2}}\ . \tag{13}$$

The equilibrium constant K here is expressed in terms of the equilibrium constants of the reaction rates. If into (13) we substitute the expression for K in terms of the standard chemical potentials, $K_r = \exp(-\sum_k \nu_k \mu_{0k}/k_b T)$, we find

$$K = \exp\left[-\left(3/2\mu_{01}^{(g)} + 1/2\mu_{02}^{(g)} - \mu_{03}^{(g)}\right)\right].$$

Equation (13) defines the thermodynamic condition for equilibrium of the system and imposes an additional relation on the equilibrium composition of the gas phase, with much the same sense at the relations considered in the theory of Gibbs phase and chemical equilibria.

As we see from (12), the concentration of the equilibrium solution is determined more by the surface of the solid in the volume than by its properties. For crystalline metals and the same gas mixtures, therefore, the equilibrium values of the surface and volume concentrations differ, depending on, e.g., what crystal plane the interface corresponds to. Moreover, these characteristics must be used to describe only equilibrium states, and not steady states in general, when the composition of the gas phase may be arbitrary. The behavior of the system under steady-state conditions is described by a kinetic model, which can be obtained by developing the hypotheses advanced in [1]. We note that the relations obtained are very important for comparison with the results from an analysis of the kinetic model at equilibrium. The fact that they coincide, i.e., that the same relations and characteristics are derived from different treatments, thermodynamic and kinetic, confirm that the models are adequate for the physicochemical process. The results can be used to analyze the processes of thermochemical treatment of materials and to assess the characteristics of the chemical reaction of atmospheres with metals and oxides in metallurgical processes.

As an example above we considered only the reaction of nitrogen–hydrogen mixtures with a condensed phase. It is easy to see that considerations entirely analogous to those above can also be used when analyzing gas mixtures with a different composition.

NOTATION

K, thermodynamic equilibrium constant; p_i, partial pressures, x_i, y_i, filling fractions of the surface layer; φ, fraction of the surface layer not filled with particles; c_*, concentration of interstices accessible to particles; ω_j, relative volume concentrations; R, number of linearly independent reactions; ξ, degree of reaction completeness; N_A, Avogadro number; ν, stoichiometric coefficient; μ, chemical potential; k_B, Boltzmann constant; T, temperature; a_i, adsorption equilibrium constants; b_i, equilibrium constants of sorption into the solid phase; K_r, equilibrium constants of chemical reaction No. r; S, component, subcomponent. Superscripts: s denotes subcomponents and k denotes components.

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