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Abstract

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METHOD FOR DETERMINING THE DEGREE OF ATOMIZATION OF A GAS IN A FLOW AND THE CATALYTIC EFFICIENCY OF METALLIC SURFACES IN ATOM RECOMBINATION PROCESSES

(Presented by Academician V. N. Kondrat' ev, 10 VII 1964)

Theoretical developments of methods for estimating the efficiency of surfaces in recombination reactions are associated with experiments carried out in a diffusion tube (Smith' s method ([1])). In particular, for this case Weiss and Eblau ([2]) considered the diffusion and heterogeneous reaction of labile particles in a cylinder of limited length; Wood and King ([3]), the case in which a tube of infinite length is replaced by a catalytic probe; and Dickens, Sheffield, and Walsh ([4]) gave a derivation and numerical solution of a three-dimensional diffusion equation. V. N. Kondrat' ev ([5]) showed that for experiments conducted in a gas jet it is also necessary to take diffusion into account.

As is known, a weak point of such experiments ([6]–[8]) is the need to determine the degree of atomization of the gas in the flow. The latter requires a considerable complication of the experimental technique (for example, Wrede' s method ([9]), the use of radiospectroscopy ([10])).

The present work makes it possible to determine directly the recombination coefficients of gas atoms on the surface of a solid body and, at the same time, the degree of atomization of the gas in the flow. In this case the thermal effects of probes may be determined, for example, by the method of Roginskii and Shekhter ([6]).

Let the velocity of motion of the flow v be directed along the x-axis. The continuity equation, taking account of the homogeneous recombination of atoms, has the form

$$D\Delta n - \frac{\partial}{\partial x}(vn) - kn^2 = \frac{\partial n}{\partial t}, \quad (1)$$

where n is the concentration, D is the diffusion coefficient of the atoms, and k is the rate constant of the homogeneous reaction.

Consider an axially symmetric problem for a cylindrical tube of diameter $2R$, with its axis coinciding with the x-axis. We shall assume that the concentration of atoms is so small that homogeneous recombination may be neglected, and that absorption of particles takes place only in two cross sections of the tube: $x = Rd$ and $x = Rl$ $(d < l)$, where the absorbing probes are located. In this case the number of particles entering a probe per unit time is equal to

$$\oint \frac{c}{4}\,\gamma n\,ds. \tag{2}$$

Here c is the mean thermal velocity of the particles, γ is the coefficient of heterogeneous recombination of atoms, and ds is an element of the probe surface. The integral is taken over the entire surface of the probe.

Assume that the probe does not disturb the moving flow (from the point of view of aerodynamics), and consider the approximation of "smearing" the probe over the cross section of the tube. We shall suppose that the probe fills the entire cross section of the tube, but in each of its elements $d\sigma$ it has a recombination coefficient $\gamma' = \gamma\,ds/d\sigma$, where ds is the part of the probe surface falling within the element $d\sigma$. Denote $ds/d\sigma = k(r)$. Then

$$\gamma' = k(r)\gamma. \tag{3}$$

The flux entering the element of the tube cross section $d\sigma$ is equal to

$$dq = \gamma' \frac{c}{4}\,n(x,r)\,d\sigma, \tag{4}$$

for $x = Rd$, $x = Rl$, and equation (1) takes the form

$$\Delta n - \frac{1}{D}\frac{\partial}{\partial x}(vn) = \frac{1}{D}\frac{\gamma c}{4}\,n(x,r)\left[k_d(r)\delta(x-Rd) + k_l(r)\delta(x-Rl)\right]. \tag{5}$$

The Dirac δ-function appearing on the right-hand side of the equation expresses the fact that we neglect the dimensions of the probes along the coordinate x. For a tube of constant cross section one may take $\partial v/\partial x = 0$. We next introduce the dimensionless cylindrical variables $\xi = x/R$, $\rho = r/R$.

$$\frac{\partial^2 n}{\partial \xi^2} - \frac{vR}{D}\frac{\partial n}{\partial \xi} + \frac{\partial^2 n}{\partial \rho^2} + \frac{\partial n}{\partial \rho}\frac{1}{\rho} =$$

$$= \frac{\gamma c}{4D} R n(\xi,\rho)\left[k_d(\rho)\delta(\xi-d) + k_l(\rho)\delta(\xi-l)\right], \tag{6}$$

$0 \le \xi < \infty$ (we consider an infinitely long tube).

Boundary conditions:

$$n(0,\rho) = n_0, \qquad \frac{\partial n(\xi,0)}{\partial \rho} = 0, \qquad n(\infty,\rho) = 0, \qquad \frac{\partial n(\xi,1)}{\partial \rho} + \theta_0 n(\xi,1) = 0, \tag{7}$$

where $\theta_0 = \gamma_0 cR/4D$, and γ_0 is the coefficient of recombination of atoms on the tube walls.

The solution of equation (6) can be obtained in the form

$$n(\xi,\rho) = \sum_i X_i(\xi) R_i(\rho), \tag{8}$$

where

$$R_i(\rho) = J_0(a_i\rho), \tag{9}$$

$$a_{iJ}1(a_i) = \theta_0 J_0(a_i). \tag{10}$$

Here $J_m(a)$ is a Bessel function of order m, $v = \text{const}$. The roots of equation (10) have been tabulated, for example, in Ref. ([2]). Introducing the notation

$$p_i = \sqrt{\frac{v^2R^2}{4D^2} + a_i^2} - \frac{vR}{2D}, \tag{11}$$

$$q_i = \sqrt{\frac{v^2R^2}{4D^2} + a_i^2} + \frac{vR}{2D}, \tag{12}$$

we obtain

$$X_i(\xi) = \begin{cases} M_i^I e^{-p_i\xi} + N_i^I e^{q_i\xi}, & 0 \le \xi \le d, \\ M_i^{II} e^{-p_i\xi} + N_i^{II} e^{q_i\xi}, & d \le \xi \le l, \\ M_i^{III} e^{-p_i\xi}, & l \le \xi < \infty, \end{cases} \tag{13}$$

where the coefficients M_i, N_i must be determined from the system of algebraic equations

$$M_i^I + N_i^I = \frac{2\theta_0 n_0}{J_0(a_i)(\theta_0^2 + a_i^2)},$$

$$M_i^{II} - M_i^I = -\left(N_i^{II} - N_i^I\right) e^{(q_i+p_i)d},$$

$$M_i^{III} - M_i^{II} = N_i^{II} e^{(q_i+p_i)l},$$

$$-M_i^I(-\theta_d + p_i) + p_{iM} i^{II} + N_i^I(\theta_d + q_i) e^{(p_i+q_i)d} - q_{iN} i^{II} e^{(p_i+q_i)d} = 0$$

(14)

$$M_i^{III}(\theta_l + p_i) - p_{iM} i^{II} + q_{iN} i^{II} e^{(p_i+q_i)l} = 0.$$

Here $\theta_d = \frac{\gamma c}{4D} R k_d$; $\theta_l = \frac{\gamma c}{4D} R k_l$. We shall assume that k_d, k_l do not depend on ρ, which corresponds to a uniform distribution of the probe turns over the cross section of the tube.

After straightforward, but rather cumbersome, calculations, the solution of system (14) is expressed in the form

$$\begin{aligned} M_i^I &= \varphi_i \left\{ q_i + p_i + (\theta_d + \theta_l) + \frac{\theta_d \theta_l}{q_i + p_i} \left[1 - e^{-(q_i+p_i)(l-d)} \right] \right\}; \\ M_i^{II} &= \varphi_i (q_i + p_i + \theta_l); \\ M_i^{III} &= \varphi_i (q_i + p_i); \\ N_i^I &= -\varphi_i \left\{ \theta_d e^{-(q_i+p_i)d} + \theta_l e^{-(q_i+p_i)l} + \frac{\theta_d \theta_l}{q_i + p_i} \left[e^{-(q_i+p_i)d} - e^{-(q_i+p_i)l} \right] \right\}; \\ N_i^{II} &= -\varphi_i \theta_l e^{-(p_i+q_i)l}. \end{aligned}$$

(15)

Here

$$\varphi_i = \frac{2\theta_0 n_0}{J_0(a_i)(\theta_0^2 + a_i^2)\Delta_i},$$

where

$$\Delta_i = q_i + p_i + \theta_d \left[1 - e^{-(q_i+p_i)d} \right] + \theta_l \left[1 - e^{-(q_i+p_i)l} \right] + \frac{\theta_d \theta_l}{q_i + p_i} \left[e^{-(q_i+p_i)d} - e^{-(q_i+p_i)l} \right] \left[e^{(q_i+p_i)d} - 1 \right].$$

(16)

Substituting (15) and (16) into (13), we obtain the atom concentrations at the points $\xi = d$ and $\xi = l$:

$$n(d, \rho) = \sum_i J_0(a_i \rho) \varphi_i \left[(q_i + p_i + \theta_l) e^{-p_i d} - \theta_l e^{-(q_i+p_i)l + q_i d} \right], \qquad (17)$$

$$n(l, \rho) = \sum_i J_0(a_i \rho)\varphi_i(q_i + p_i)e^{-p_i l}. \tag{18}$$

The flux (2) of particles entering the probe in the cross section ξ of the probe location, and the thermal effect of the probe, are respectively equal to

$$q_\xi = \pi R^2 \frac{\gamma c}{2} k_\xi \int_0^1 n(\xi, \rho)\rho \, d\rho; \qquad Q_\xi = \frac{E_d}{2} q_\xi.$$

Here E_d is the dissociation energy of the gas molecule.

These expressions, as well as (16), (17), and (18), give in the cross sections $\xi = d$ and $\xi = l$:

$$Q_d = \frac{E_d}{2}\pi R^2 \theta_0^2 \gamma c k_d n_0 \sum_i e^{-p_i d} \frac{p_i + q_i + \theta_l \left[1 - e^{-(q_i+p_i)(l-d)}\right]}{a_i^2(\theta_0^2 + a_i^2)\Delta_i}, \tag{19}$$

$$Q_l = \frac{E_d}{2}\pi R^2 \theta_0^2 \gamma c k_l n_0 \sum_i e^{-p_i l} \frac{q_i + p_i}{a_i^2(\theta_0^2 + a_i^2)\Delta_i}. \tag{20}$$

The quantities Q_d and Q_l are determined experimentally. Consequently, (19) and (20) represent a system of two algebraic equations with respect to two unknown quantities: the recombination coefficient γ and the atom concentration n_0. This system, generally speaking, does not permit a closed-form solution, because it includes infinite sums, though rapidly convergent ones. By restricting oneself to a finite number of terms, the equations can be solved to any desired degree of accuracy.

In accordance with the proposed method, experiments were carried out to study the recombination of hydrogen atoms on the surface of pure copper at a gas pressure of 0.194 mm Hg. Mesh probes made of wound spirals of copper wire 0.17 mm in diameter filled the corresponding cross sections of a quartz tube of radius 8 mm at distances of 22 and 38 mm from the discharge tube.

The thermal effects of the probes, determined analogously to (6), at a probe temperature of 75°, were respectively 0.1920 and 0.0605 J. In calculating the quantities γ and n_0 according to (19) and (20), values of the coeff-

diffusion coefficient of atomic hydrogen in molecular hydrogen, calculated analogously to (11), $D = 8.23 \cdot 10^3$ cm^2/s, the coefficient of recombination of hydrogen atoms on the surface of quartz $\gamma_0 = 1.2 \cdot 10^{-4}$, taken from (12), and the jet velocity $v = 58.4$ cm/s (determined experimentally). The desired quantities obtained in this case are: $\gamma_{\mathrm{H}}/c_{\mathrm{u}} = 4.65 \cdot 10^{-2}$, $n_0 = 1.46 \cdot 10^{14}$ atoms/cm^3, and the degree of atomization of the gas at the entrance to the reaction tube is 2.58%.

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Note: Figure translations are in progress. See original paper for figures.