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#### DIFFUSION SEPARATION OF HYDROGEN FROM GAS MIXTURES

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Experiments are described and a model is evaluated for the process of production of superpure hydrogen from mixtures with ammonia and nitrogen by selective diffusion through thin metallic membranes.

Current predictions indicate that the worldwide demand for hydrogen for use in energy production and industry will increase by a factor of at least 4-5 times by the end of the present century [1, 2]. In a number of industries (foremost ferrous metallurgy and chemical technology) there is an increasing need for hydrogen of very high purity (more than 99.999%).

In principle hydrogen of such high purity can be obtained either by the conventional electrolytic method, or by using selective diffusion through membranes of palladium and its alloys [3-5]. In contrast to the majority of other metals, glasses, polymers, etc., those materials are highly permeable to hydrogen, while remaining practically impermeable to other gases [6]. Among the advantages of the diffusion method are simplicity of construction, easy mobility and long lifespan of the equipment, low cost, high (up to 99.9999%) purity of the product, simplicity, and safety in use [7, 8]. Calculations performed with data from experimental industrial tests of diffusion equipment indicate that the unit cost of hydrogen produced by this method in equipment operating at the 500-1000 m<sup>3</sup>/h level is 40-70 rubles/1000 m<sup>3</sup>, i.e., 2-3 times less expensive than hydrogen produced electrolytically, while having a significantly higher purity.

At the present time the diffusion method is used for hydrogen production in a wide range of small scale (up to 100 m<sup>3</sup>/h) devices. Attempts to design and utilize larger-scale separators based on tube type diffusion cells (undertaken mainly in the USA) have not met with success, due to technological unreliability of diffusion cell construction and losses related to cell combination. The latter is to a great degree the result of difficulties in mathematical modeling of the mass-exchange processes in real diffusion separators with consideration of inhomogeneity in mixture composition and pressure in the cells, hydraulic resistance, etc. Examples of theoretical studies can be found in [9-11].

New possibilities for development of large-scale diffusion technology have appeared as a result of multifaceted studies of metal physics and welding technology which have made possible construction of high-output diffusion cells with highly reliable sealing properties. The equipment in which these cells are used consists of a group of alternating supply and output channels, separated by thin walls which are permeable only to hydrogen. In the present study we will consider hydrogen diffusion separation in cells with planar channels

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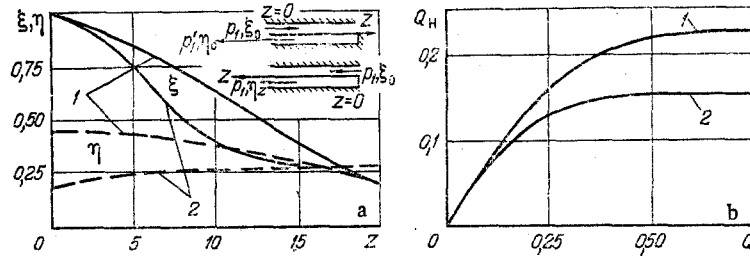


Fig. 1. Calculated distributions of hydrogen partial pressures in supply and output channels (a, solid and dashed lines respectively) and diffusion cell output (b): 1, forward flow; 2, reverse flow;  $\eta_* = 0.2$ ;  $\beta = 0.5 \cdot 10^{-2}$ ;  $p = 1.0$  MPa;  $p'_* = 0.15$  MPa;  $LP = 2.94 \cdot 10^{-2}$  m<sup>2</sup>;  $T = 630^\circ\text{C}$ .

with walls formed of palladium alloyed with silver, gold, platinum, and rubidium [6] at an operating temperature of  $630^\circ\text{C}$ . A gas mixture containing free hydrogen is pumped through the supply channel system, and the free hydrogen diffuses through the walls to the output channels.

To analyze such systems it is sufficient to consider an isothermal system of two parallel channels of constant cross section, filled respectively by the compressed mixture undergoing separation, and by hydrogen. (A sketch of the channels for forward and reverse flow is shown in Fig. 1a.) In the general case the intensity of hydrogen separation into the output channel depends on mixing of the components in the input channel, transport of hydrogen to the wall, its adsorption and solution, diffusion of the dissolved hydrogen, desorption, and liberation into a collector joining the output channels. It was shown by preliminary laboratory experiments that in separation of hydrogen from a nitrogen-hydrogen mixture at a temperature above  $450^\circ\text{C}$  and partial hydrogen pressure greater than 0.5 MPa, the limiting stage of the mass-exchange process is the transfer of the hydrogen through the wall. In the experiments considered the hydraulic resistance of the supply channels was negligibly small, and there was practically no chemical interaction in the gas mixtures used.

Therefore, the simplest variant of the model proposed in [12] was sufficient, in which chemical reaction in the mixture is completely neglected. In dimensionless form the basic equations the solutions of which completely describe the mass-exchange process have the form:

$$\frac{d\xi}{dz} = -(1 - x_0\xi)^2 (V\bar{\xi} - V\bar{\eta}), \quad \frac{d^2\eta}{dz^2} = -\beta (V\bar{\xi} - V\bar{\eta}). \quad (1)$$

Here we use the well-known Sivert's law for solubility of a dissociated biatomic gas in a solid material and introduce the following dimensionless quantities:

$$\xi = \frac{x}{x_0}, \quad \eta = \frac{p'}{x_0 p}, \quad z = \frac{Pk}{Sj_c} \sqrt{\frac{p}{x_0}} l, \quad (2)$$

$$\beta = \frac{\alpha SMj_c^2}{Pk p} \sqrt{\frac{x_0}{p}}, \quad Z = \frac{Pk}{Sj_c} \sqrt{\frac{p}{x_0}} L.$$

The hydraulic resistance coefficient in the output channel is introduced in accordance with the equation of conservation of momentum, written in the form  $dp'/dl = -\alpha\rho'v'$ .

The boundary condition for  $\xi(z)$  is obvious: at the input to the supply channel, i.e., at  $z = 0$ , we have  $\xi = 1$ . The boundary conditions for  $\eta(z)$  depend on the flow organization in the channel under consideration. Forward and reverse flow in the output channel (where the sections  $z = 0$  and  $z = Z$  are sealed, respectively) correspond to the conditions:

$$\left. \frac{d\eta}{dz} \right|_{z=0} = 0, \quad \eta|_{z=Z} = \eta_*; \quad (3)$$

$$\eta|_{z=0} = \eta_*, \quad \left. \frac{d\eta}{dz} \right|_{z=Z} = 0,$$

where  $Z$  corresponds to the output section of the supply channel and the dimensionless pressure  $\eta_*$  characterizes the hydraulic losses in the tract connecting the channel to the collector, as well as the pressure in the collector.

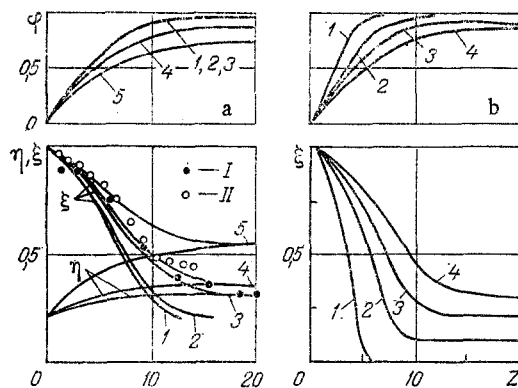


Fig. 2. Productivity  $\varphi$  versus  $Z$  and distributions of dimensionless pressures  $\xi$  and  $\eta$ : a) counterflow,  $\eta_* = 0.2$ ;  $\beta = 0, 0.001, 0.0076, 0.01, 0.02$  (curves 1-5); points, experiment at  $p = 0.868$  MPa;  $p'_* = 0.13$  MPa,  $Q_H = 0.153$  and  $0.34$  m<sup>3</sup>/h (I and II, respectively); b)  $\beta = 0$ ;  $\eta_* = 0, 0.1, 0.2, 0.3$  (curves 1-4).

The problem of Eqs. (1), (3) was solved numerically by the Runge-Kutta method. Figure 1a shows calculations of the distribution of dimensionless partial hydrogen pressure along the supply and output channels. Comparison of these distributions for the cases of forward and reverse flows with other conditions equal shows that in the forward flow cell diffusion of the liberated hydrogen through the semipermeable wall is accomplished at higher pressures  $\eta$  in the larger portion of the output channel, while reduction of hydrogen partial pressure in the supply channel occurs less intensely than in the counterflow cell. A comparison of productivities (hydrogen output) of diffusion apparatus using the forward and reverse flow methods agrees with this conclusion. Figure 1b shows the dependence of hydrogen liberation rate  $Q_H$  in one of the cells used upon total flow rate of a mixture of hydrogen with ammonia and nitrogen (dissociated ammonia)  $Q$ , as obtained by calculations with the model used here. As the input flow rate is increased, the significant advantage of the counterflow system manifests itself. As low as  $Q = 0.25$  m<sup>3</sup>/h the forward flow cell reaches maximum output, which remains practically the same for further increase in  $Q$ ; in regimes of practical interest, this cell proves to be about 1.5 times less productive than a similar counterflow cell. We note that the superiority of counterflow flow organization in diffusion separation apparatus to forward flow systems has been observed previously (see, for example, [9, 10]).

To study the characteristics of operation of diffusion cells and large-scale equipment composed of such cells, it will be convenient to introduce the relative productivity function

$$\varphi = 1 - \frac{j_H(Z)}{j_H(0)} = \frac{1 - \xi(Z)}{1 - x_0 \xi(Z)} \quad (4)$$

Calculated dependences of  $\varphi$  on the dimensionless length of a counterflow cell for various  $\beta$  are shown in Fig. 2a. Also shown there are corresponding distributions of dimensionless pressures  $\xi$  and  $\eta$ , as well as characteristic experimental data.

The difference between forward and counterflow disappears at "zero" hydraulic resistance of the output channel ( $\beta = 0$ ). Increase in  $\beta$  markedly lowers the productivity of counterflow, but especially, forward flow systems. Determination of the value of  $\beta$ , which together with  $Z$  affects the relative productivity of the system, by direct flow measurements in the output channel is difficult. Apparently it is always more convenient to determine the value by comparing experimental data on the distribution of, for example, partial hydrogen pressure in the supply channel, to calculated data obtained for various  $\beta$  values.

Figure 2b shows the results of calculations for the optimal case of  $\beta = 0$  for various supply line pressures. The curves for  $\eta_* = 0$  correspond to the system with maximum possible separation efficiency (separation of hydrogen into a vacuum), all other conditions being equal.

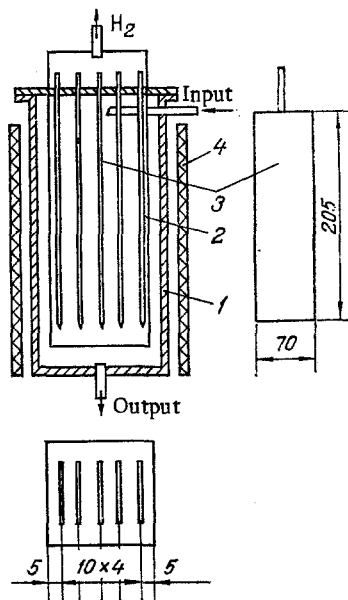


Fig. 3

Fig. 3. Laboratory arrangement. 1) Container; 2) shell; 3) diffusion element (cell); 4) heater. Dimensions in mm.

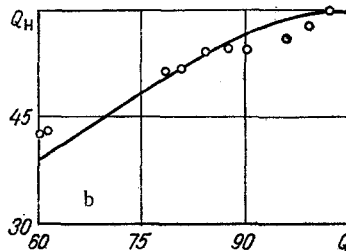
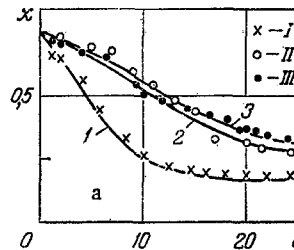


Fig. 4

Fig. 4. Distribution of molar fraction of hydrogen  $x$  in supply channels of laboratory arrangement (a) and output of experimental industrial arrangement versus dissociated ammonia flow rate (b). Points, experiment; curves, theory. a)  $p \approx 0.85$  MPa;  $Q_H = 0.153, 0.340$  m<sup>3</sup>/h at  $p'_* = 0.13$  MPa (I, II, respectively);  $Q_H = 0.242$  m<sup>3</sup>/h,  $p'_* = 0.20$  MPa (III); b)  $p = 1.0$  MPa,  $p'_* = 0.125$  MPa,  $T = 600^\circ\text{C}$ .  $l$ , cm;  $Q_H, Q$ , m<sup>3</sup>/h.

The calculation model was adjusted using experimental data obtained with a laboratory arrangement consisting of a high-purity hydrogen diffusion system, equipment for producing dissociated ammonia (25% nitrogen, 75% hydrogen) and a monitoring and control system. The initial mixture used in the experiments was dissociated ammonia, prepared by gasification of liquid ammonia at a pressure of 0.6–1.0 MPa with subsequent practically total dissociation of the gas in a KDA-10 catalyzer at the same pressure and a temperature of 650–800°C. (By varying the temperature the residual ammonia content could be varied if necessary.) In some of the experiments special purity nitrogen was mixed into the dissociated ammonia; in this case the nitrogen content was controlled automatically by a chromatographic system. The same system monitored the hydrogen content of the gas fed to the supply system. The flow rate of the gases exiting the channels was measured by rheometers or RS-3A rotameters, calibrated against reference gas meters or flow rate meters. The purity of the hydrogen obtained was monitored by a chromatograph with three-stage "Mikrokhrom" accumulator with the capability of resolving nitrogen to 10<sup>-7</sup>%, and also by electrochemical oxygen potential sensors.

The hydrogen diffusion system used either three or five planar diffusion cells, located in a cylindrical container placed with a furnace held at the desired temperature. Figure 3 shows a simplified sketch of the laboratory system; the working cells were installed at identical distances of 10 mm from each other and enclosed by a shell to make the geometry the same as the computation model. After preheating the initial gas mixture was supplied to the upper portion of the container and pumped down along the diffusion elements (dimensions 205 × 70 mm); the processed mixture was removed for measurement and disposal. Hydrogen concentration along the length of one supply channel (the central one in the container) was measured in three series of experiments. For this purpose a stainless-steel capillary tube was moved along its length using a special gasket. This tube was used to supply samples to a "Gazokhrom-3101" chromatograph through a special valve, with sampling periods being as short as possible to minimize gasdynamic distortions. Between experiments the container was filled with argon or high purity nitrogen, and the internal cavities of the cells were

TABLE 1. Comparison of Methods for Determination of Output from One 750 × 140 mm Diffusion Element or Two 375 × 140 mm Elements (n, number of elements in unit)

Output from [6], m <sup>3</sup> /h	Output by model of present study, m <sup>3</sup> /h		Exptl. output, m <sup>3</sup> /h
	750×140 mm, n = 59	375×140 mm, n = 118	
1,66	0,99 0,87	1,14 0,96	0,95 0,87

TABLE 2. Effect of Initial Mixture Pressure on Hydrogen Generation Efficiency

Dissociated ammonia pressure, MPa	1,00	1,25	1,50	1,75	2,00
Partial hydrogen pressure at output, MPa	0,56	0,53	0,54	0,53	0,56
Dimensionless hydrogen concn. at output	0,74	0,57	0,48	0,40	0,37
Rel. productivity	0,59	0,72	0,82	0,85	0,85

evacuated. In 4 years of testing the unit underwent about 120 thermal cycles to a working temperature not less than 630–650°C with no loss of hermeticity. It was found that presence of ammonia in the initial mixture (in some cases its molar content reached 30%) had no effect on the output of the unit, permitting a reduction in the degree of dissociation required, which will significantly simplify industrial scale units.

Figure 4a shows results of partial pressure measurements along the container length, and theoretical curves corresponding to the conditions realized in experiment. For the three series of experiments shown in Fig. 4a good agreement between theory and experiment was achieved at one and the same value of  $\beta = 0.8 \cdot 10^{-2}$ , which also indicates the adequacy of the model used.

In the case of forward flow the agreement between theory and experiment proved to be significantly worse, especially at low mixture flow rates. Hydrogen concentration in the container proved close to homogeneous and approximately equal to the value determined from the condition of global mass balance for the container as a whole. This concentration equalization, which occurs with a significant loss of hydrogen through the membrane, is apparently caused by convective flows in the container which develop because of differences in densities of the mixtures enriched by hydrogen to different degrees (in the forward flow experiments the mixture was pumped from bottom to top, i.e., in the absence of convection the mixture density in the upper part of the container would be higher than in the lower). The theory developed in [12] and used herein does not consider this effect: it completely neglects axial mixing in the supply channels.

The experimental results permit a number of recommendations for practical organization of the process of hydrogen separation from inert mixtures with other gases. To verify the suitability and adequacy of the design solutions used, the DB-100 experimental industrial unit was designed, constructed, and placed in use under industrial conditions (in a tube plant) to produce industrial quantities of high-purity hydrogen from dissociated ammonia. The unit consists of a container with inner diameter of 350 mm, 950 mm long, containing 59 all-welded planar diffusion elements, similar to those described above, with dimensions of 750 × 140 mm. As in the laboratory experiments the membrane material was an 0.1-mm-thick foil of V-1 palladium based alloy. In order to efficiently fill the working volume, the diffusion elements were spaced every 5 mm. In the design of this unit data from [6] were used, allowing determination of the total separation membrane area required for the desired output on the basis of effective permeability coefficient measurements performed on the V-1 alloy. The unit was designed for an output of 100 m<sup>3</sup>/h with consideration of the counterpressure produced by the consuming device. However, tests revealed a markedly lower output (as low as 78 m<sup>3</sup>/h even without counterpressure), due to inaccuracies of the simple diffusion model used in [6] to predict output.

Analysis of the laboratory and industrial data obtained together with the consequences of the model considered here have allowed an analysis of the errors introduced in design of

the industrial unit in arrangement gas flows in the supply and output channels. Table 1 shows a comparison of actual output obtained from the DB-100 unit in two of the regimes studied with results of calculations using the model of [6] and the model of the present study. It is evident that neglect of gas mixture inhomogeneity, as in [6], leads to an error in calculating output by a factor of more than 1.5 times.

Results of testing the DB-100 industrial unit in one operating regime are shown in Fig. 4b. Good agreement between theory and experiment in this and other regimes was obtained at values of  $\beta = 0.18 \cdot 10^{-1}$ . As an additional illustration of the capabilities of the present model, Table 2 presents a calculated analysis of the effect of total mixture pressure on relative productivity of a unit with geometric parameters of the supply portion similar to those of the DB-100. It is clear that the initial mixture pressure cannot be selected arbitrarily, but must be determined so as to obtain the required productivity. In particular, for a DB-100 type unit, increase in pressure above 1.5 MPa leads to practically no increase in output. With such approaches it has become possible to solve the problem of determining the optimum choice of compressor equipment for use with industrial hydrogen diffusion separation systems. Thus for systems designed to produce especially pure hydrogen standard 1.8 MPa gas compressors are suitable, while systems which evacuate the inner cavity can use even higher pressure.

Use of the model presented in [12] and the present study has allowed development of hydrogen diffusion separation equipment with 80% higher unit power with no increase in use of precious metals.

#### NOTATION

$j_H, j_C$ , molar fluxes of hydrogen and ballast gas;  $k$ , effective permeability coefficient (product of hydrogen solubility coefficient times diffusion coefficient, divided by membrane thickness);  $l, L$ , coordinate measured along supply channel and maximum value thereof (channel length);  $M$ , molecular weight of hydrogen;  $P$ , working perimeter of diffusion cell;  $p, p'$ , pressure in supply and output channels;  $Q, Q_H$ , mixture flow rate and hydrogen output for one cell or entire unit;  $S$ , area of working section of supply channel;  $v'$ , velocity in output channel;  $x, x_0$ , molar fraction of hydrogen in mixture and value thereof at inlet;  $z, Z$ , dimensionless coordinate and length of apparatus;  $\alpha, \beta$ , dimensional and dimensionless hydraulic resistance coefficients;  $\eta, \eta_*$ , dimensionless pressure in output channel and value thereof at outlet;  $\xi$ , dimensionless pressure (concentration) of hydrogen in supply channel;  $\rho'$ , hydrogen density in output channel;  $\varphi$ , relative output.

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