Physical Chemistry

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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

Full Text

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On the Elementary Stages of the Process of Recombination of Hydrogen Atoms on the Surface of Aluminum

Activation Energy of the Reaction

To elucidate the nature of the effectiveness of a solid surface in reactions of heterogeneous recombination of atomic gases, it is extremely interesting to study the catalytic behavior of both transition and nontransition metals.

As is known ([1,2]), in a number of reactions the greatest catalytic activity is possessed by metals in which the total number of *s*- and *d*-electrons exceeds the number of electrons participating in the metallic bond. The maximum of catalytic activity in this case corresponds to a definite number of unpaired *d*-electrons, different for different reactions. If one follows the established views and takes into account only this circumstance ([4]), then one may expect a decrease in the recombination coefficients of hydrogen atoms on aluminum (a nontransition metal) in comparison with the platinum studied by us earlier ([3]).

Fig. 1. Dependence of the number N_r of hydrogen atoms recombining on Al on the wire temperature at values of P_H:
1—$0.7 \cdot 10^{-2}$, 2—$1.14 \cdot 10^{-2}$, 3—$1.94 \cdot 10^{-2}$, 4—$3.5 \cdot 10^{-2}$, 5—$4.69 \cdot 10^{-2}$ mm Hg.

Fig. 2. Temperature dependence of the recombination coefficients of hydrogen atoms on aluminum for partial pressures P_H:
I—$4.69 \cdot 10^{-2}$; II—$3.5 \cdot 10^{-2}$; III—$1.94 \cdot 10^{-2}$; IV—$1.14 \cdot 10^{-2}$; V—$0.54 \cdot 10^{-2}$ mm Hg.

In the present work, the kinetics of recombination of H atoms on Al was investigated by the method described earlier ([3,5]), using the differential compensation method of Roginskii—Shekhter. The rate of the recombination reaction was studied in the range of partial pressures of H atoms from 0.005 to 0.05 mm Hg and temperatures from 20 to 450° C, at a velocity of the atom-entraining jet of 10 m/sec and an average content of $\sim$ 10% atoms in the atomic-molecular stream from the glow-discharge tube. An Al wire of $d = 0.1$ mm was used as the catalyst, containing, according to spectral analysis, Al—99.97%, Fe 0.01%, Mg 0.01%, Si 0.005%, Mn, Cr, and Cu 0.001% each. The quantity N_r of hydrogen atoms reacting per unit time per unit geometric surface area of the catalyst at various

temperatures of the surface and gas pressures in the system is presented in Fig. 1. Figure 2 gives, in the form most convenient from the standpoint of the theory of absolute reaction rates, the temperature dependence, calculated on the basis of experimental data, of the probability of the γ-process of recombination as a result of effective impacts of atoms arriving from the volume on those chemisorbed at "active sites" of the aluminum surface. In accordance with transition-state theory, this dependence is expressed by the equation

$$\gamma = \frac{\chi C_s[1 - f'(\theta)]h^2}{2\pi mkT}\, e^{-600/RT} \tag{1}$$

with different values of the product of the transmission coefficient χ and the average number of H atoms chemisorbed on 1 cm^2 of the Al surface (at different pressures—from $7.7 \cdot 10^{14}$ to $5.13 \cdot 10^{15}$). At the same time, over the entire interval P_H, a rather constant value is observed for the apparent activation energy, $E = 600$ cal/mole. We note here also that, according to the data of work (^{6}), the process of hydrogen recombination on Al generally requires no activation energy.

As is seen from Fig. 2, the probability of recombination decreases noticeably with increasing partial pressure of the reacting atoms, which causes a deviation of the reaction rate from the first-order equation. It is interesting, further, to compare the numerical values obtained for the coefficients γ for hydrogen on the aluminum and platinum surfaces studied by us, for example, at $P_H = 1.94 \cdot 10^{-2}$ mm Hg (Table 1).

Table 1

Values of the coefficients $\gamma \cdot 10^2$ for hydrogen

Metal	80°	110°	160°	210°	240°	280°	410°
Al	2.6	3.7	4.4	5.1	5.0	4.9	3.5
Pt	1.3	1.6	2.5	4.7	6.7	7.0	8.7

From the data of Table 1 it is seen that, up to the temperature at which noticeable desorption of adsorbed atoms from the catalyst surface begins (ascending

Fig. 3. Motion of the representative point corresponding to heterogeneous recombination of atoms

Figure 3: Fig. 3. Motion of the representative point corresponding to heterogeneous recombination of atoms

Fig. 4. Curve of the profile of the reaction path

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branches of the curves in Fig. 1), owing to the action of certain factors determining the kinetics, the efficiency of recombination on the nontransition metal (Al) is considerably higher than that on the transition metal (Pt). The role of these factors can be understood only by presenting in detail the mechanism of the process in the course of the reaction.

Fig. 3. Motion of the representative point corresponding to heterogeneous recombination of atoms

Since recombination reactions are exclusively exothermic, removal of the energy with the aid of a third particle is highly significant. Only in the case of triple impacts do inelastic collisions of atoms and the formation of an activated complex take place. Obviously, the degree to which the metal atom Me is capable of facilitating the reaction of combination of hydrogen atoms depends on the shape of the potential-energy surface (Fig. 3) for the case when the Me and H atoms can interact chemically. Consequently, it depends both on the magnitude of the heat of chemisorption Q of the H atom on the given surface (the depth of the valley $\mathrm{MeH} + H$, parallel to the abscissa axis), and on the height of the ridge that separates this valley from the valley of the final state $\mathrm{Me} + H_2$, corresponding to the minimum of the potential energy of the system.

On the vertical section of the potential surface along the reaction coordinate (Fig. 4), the degree of advance of the system is clearly illustrated

along the reaction path. In this case the energy difference between the initial and final states of the system is equal to the dissociation energy of the molecule H_2, while the energy difference corresponding to the saddle point of the transition state $\mathrm{Me} \cdot\cdot \mathrm{H} \cdot\cdot \mathrm{H}$ and the state of chemisorption equilibrium represents the minimum energy E, whose expenditure from outside is necessary for the occurrence of elementary acts of the reaction. In accordance with Fig. 4, in the course of the reaction the system must overcome two energy barriers. Usually, in the case of nonactivated chemisorption $E_{\mathrm{ads}} = 0$, and therefore the probability of the γ-surface reaction is determined by the relation between the quantities Q and E.

Fig. 4. Curve of the profile of the reaction path

Let us next consider the question of the physical content of the quantity E, which is, in a certain sense, a measure of the catalytic properties of one material or another. It is easy to imagine that, in an effective triple collision, absorption of the energy necessary to overcome the barrier E can occur only at the expense of a corresponding transformation of the kinetic energy of the atom arriving from the bulk as it "sticks" to the surface. In this case an algebraic redistribution of E_{kin} takes place between the two remaining collision partners—the atom of the solid (the energy of the intrinsic vibrations in the crystal lattice) and the chemisorbed atom. As a result, the latter receives the energy for the creation of an additional bond and the formation of a labile complex Me •• H •• H with an excess of internal or kinetic energy.

Taking into account only these simple considerations, and also neglecting the additional velocities of the atoms due to the jet velocity u_2 (in our case an error of up to 1%) and considering only the thermal velocities u_1 of the atoms, we obtain, in the calculation per 1 mole of reacting gas:

$$\frac{M(u_1+u_2)^2}{2} = \frac{3}{2}RT_{\text{eff}} = b(T)R\theta_D + E. \tag{2}$$

Here θ_D is the characteristic Debye temperature, T_{eff} is a certain effective temperature corresponding to the heat distribution near the surface of the heated metal (at distances up to the magnitude of the mean free path, determined by the kinetic conditions in the gas); $b(T)R\theta_D$ is the energy of vibrations of the crystal lattice.

In accordance with Grüneisen' s formula (7) for characteristic temperatures, the equation (4) of work (3), cited earlier for calculating the coefficient γ of heterogeneous recombination, can be written in the form:

$$\gamma = \frac{\varkappa\left(C_s - \dfrac{U'he^{Q/RT}}{kT}\right)h^2}{2\pi mkT}e^{-b'(T)\left[\frac{3}{2}T_{\text{eff}} - \frac{9.9}{a^{1/3}v^{1/3}}\left(\frac{C_p}{\alpha}\right)^{1/2}\right]/T}. \tag{3}$$

Thus, the conditions for recombination of atoms on the surface of a catalyst, especially for temperatures below noticeable desorption, are substantially affected by the following physical parameters of the metal: the coefficient a of atomic packing density, the specific heat C_p at constant pressure, the atomic volume v, and the coefficient α of thermal expansion.

If these circumstances are taken into account, as well as the fact that, according to our data, at $P_H = 1.94 \cdot 10^{-2}$ mm Hg the temperature maximum of the $N_r(t)$ curve for an Al catalyst corresponds to 230°C, whereas for Pt it is 580°C, it is not difficult to understand the course of the experimental data in Table 1. Higher val—

The values of $\gamma_{\text{H/Al}}$ in comparison with $\gamma_{\text{H/Pt}}$ (up to the temperature $T_{\max}$) are apparently explained by the larger value of θ_D for Al and, consequently, by the smaller value of the activation energy E. Our data agree with the results of Wise and Wood (6) in that the high efficiency of recombination on a solid can be exhibited by materials of low compressibility, characterized by a high propagation velocity of longitudinal and transverse lattice waves.

The decrease in $\gamma_{\mathrm{H/Al}}$ with increasing gas pressure in the system can be explained by a decrease in the value of the coefficient χ entering into equation (3).

At high rates of the recombination process (values of P_H up to 0.05 mm Hg —see Fig. 1) and the liberation of extremely large amounts of heat—above a certain critical value—energy transfer becomes less effective. It is precisely the decrease in thermal accommodation as a result of insufficiently rapid removal of energy that apparently accounts for a certain probability that a system possessing enough energy to reach the activated state nevertheless returns to the initial state (MeH+H). In other words, the value of the transmission coefficient for the case of recombination of atomic gases is determined by the contact time of the activated complex $\mathrm{Me \cdot H \cdot H}$ with the catalyst surface. Complete heat exchange can occur only when the residence time of the complex on the surface-active catalytic center (the delay time) exceeds the period of oscillation of the atoms of the solid by at least two orders of magnitude.

Thus, in accordance with transition-state theory and equation (3) presented above, an understanding of the nature of heterogeneous recombination of atoms is impossible without taking into account a number of micro- and macroscopic factors and, in particular, certain physical properties of the solid catalyzing the reaction.

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