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Academician of the Academy of Sciences of the Ukrainian SSR I.
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Fig. 1

Figure 1: Fig. 1

Abstract**Full Text***PHYSICAL CHEMISTRY*

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RECOMBINATION OF HYDROGEN ATOMS ON THE SURFACE OF PLATINUM

In recent years interest has grown in the study of processes of heterogeneous recombination of atomic gases on solid surfaces and coatings. In some works ^(1,2) complete recombination of hydrogen atoms on platinum is assumed, at least at temperatures up to 750–800°, which would open the possibility of using a platinum catalyst as an absolute standard for the number of atoms perishing in collisions. Equality of the recombination coefficient to unity apparently cannot in general be consistent with the mechanism of the process proposed by V. N. Kondrat'ev in ⁽³⁾, where the picture of homogeneous recombination in collisions of three bodies is considered. The extreme inconsistency of the available literature data ^(2,4,5,7), as well as the absence of a detailed study, is noteworthy.

Fig. 1

In the present work we present the results of our investigation of the recombination of H atoms on Pt under conditions of generation of up to 10% atoms in a high-voltage discharge tube with electrodes of pure aluminum, $U = 3000$ V, from which they were extracted by means of a jet; the flow velocity was determined from the gas consumption, which was 8 ml/min. The catalyst, in the form of a resistance thermometer made of wire 0.1 mm in diameter, was placed in a plane perpendicular to the direction of the flow. The collision efficiency coefficient γ and the number of atoms that had reacted, N_r , were determined by the method of calculating the thermal energy of recombination on wires according to S. Z. Roginskii and A. B. Shekhter ⁽²⁾. The accuracy of determining the temperature dependence of γ by this method considerably exceeds the accuracy of the corresponding determination of γ from the thermoe.m.f. of a thermocouple probe, calculated using the so-called diffusion method of Smith's "movable sample" for a side tube ^(1,6). Measurements were carried out by us for the temperature interval 25–850° and the pressure interval $P_{\text{H}_2} = 0.05\text{--}0.2$ mm Hg; the latter excluded the possibility of parallel occurrence of homogeneous recombination. Reproducibility of the results was achieved by treating the glass

Fig. 2

Figure 2: Fig. 2

part of the apparatus with a 1% borax solution (to reduce to a minimum the death of atoms on the vessel walls), and also by preliminary bombardment of the resistance thermometer with H atoms when placing it in the discharge tube for 1–2 hours before each experiment, which apparently is connected with the need to establish the corresponding adsorption equilibrium.

Over the entire temperature interval studied, the kinetics of the recombination reaction of H on Pt follows first order. Thus, each gas-phase atom arriving at the surface and reacting with a chemisorbed atom has a definite constant probability of reaction, independent of pressure. The exothermic process of heterogeneous recombination is represented as consisting of two stages: 1) chemisorption of atoms on the surface of a solid and 2) recombination of atoms as a result of an effective collision of an atom from the volume with one adsorbed on the surface.

Fig. 2. Number of recombining hydrogen atoms at partial pressures of atomic gas (in mm Hg): 1 $-5.4 \cdot 10^{-3}$; 2 $-7.0 \cdot 10^{-3}$; 3 $-1.14 \cdot 10^{-2}$; 4 $-1.94 \cdot 10^{-2}$.

In accordance with the theory of absolute reaction rates⁽⁸⁾, if the chemisorbed activated complex on the platinum surface is represented in the form Pt–H–H, then the recombination coefficient is

$$\gamma = \frac{C_g C_s (kT/h) (f^\ddagger / F_g f_s) e^{-E/RT}}{C_g (kT/h) (f^\ddagger / F_g)}, \quad (1)$$

where C_g is the concentration of H atoms in the gas volume; C_s is the number of chemisorbed atoms per 1 cm² of platinum surface; f^\ddagger , f_s , and F_g are, respectively, the complete distribution functions of the activated complex Pt–H–H, of the chemisorbed atom Pt–H, and of the gas-phase hydrogen atom (per unit volume of the reacting gas), and E is the activation energy of the recombination process.

Hence, if the activated complex and the chemisorbed atom possess the same degrees of freedom, it is not difficult to obtain the expression

$$\gamma = \frac{C_s h^2}{2\pi m k T b_g} e^{-E/RT}, \quad (2)$$

where m is the mass of the hydrogen atom; b_g is the distribution function for rotation and vibration of the gas-phase reactant.

Since, upon chemisorption of atomic gases, the adsorbate possesses neither rotational nor vibrational energy, $b_g = 1$. The graphical dependence $\ln(\gamma T) = f(1/T)$ (Fig. 1), obtained by us for a partial pressure of H atoms equal to

$1.94 \cdot 10^{-2}$ mm (the thermistor was located at a distance of 3 mm from the discharge) in the temperature range 25–900°, leads to the equation

$$\gamma = \frac{4.9 \cdot 10^{15} h^2}{2\pi m k T} e^{-1260/RT}. \quad (3)$$

According to the data of Wood and Wise ⁽⁵⁾, $E = 1040$ cal/mole. This value agrees well with our value of the apparent activation energy; however, the very large scatter of the points obtained by the authors ⁽⁵⁾ is due to incorrect construction of the graph itself from the point of view of the theory of absolute reaction rates.

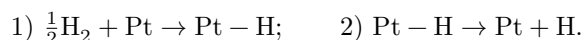
Calculated on the basis of our experimental measurements by the method of Roginsky and Shekhter ⁽²⁾, the temperature dependences of the number of reacted hydrogen atoms N_r at different gas pressures in

system are shown in Fig. 2. In this case

$$N_r = \frac{\Delta W \cdot 2 \cdot 6.06 \cdot 10^{23}}{S \cdot D} \text{ atoms} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1},$$

where ΔW is the difference between the electrical-heating powers of the platinum wire required to maintain the same temperature under conditions of absence of recombination and of its occurrence (with the other reaction conditions kept constant); S is the surface area of the catalyst; $D = 4.32 \cdot 10^5$ W · sec is the dissociation energy of one mole of hydrogen molecules.

The decrease in the recombination coefficient γ with increasing temperature, beginning at 400–600° (Fig. 2), indicates the simultaneous occurrence of a strongly endothermic process of desorption of H atoms from Pt, or of atomization of molecular hydrogen on the heated wire. The latter, naturally, requires a higher activation energy and, in turn, includes the stage of desorption of atoms according to the scheme:



As Brennen and Fletcher ⁽⁹⁾ showed, the overall rate of atomization of hydrogen on platinum is proportional to the square root of the partial pressure of the gas. We, however, observe (Fig. 2), with increasing gas pressure, a shift of the maximum of the $N_r(T)$ curve toward higher temperatures. If one also takes into account, for the atomization scheme given above, the necessity of free mobility of the adsorbed Pt–H atom, one may conclude that the kinetics of recombination are complicated only as a result of the occurrence of the process of desorption of H atoms.

Fig. 3. Calculation of the quantity Q from equation (5)

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Fig. 4. Fraction of the platinum surface covered with chemisorbed hydrogen atoms ($P_H = 1.94 \cdot 10^{-2}$ mm Hg).

Figure 4: Fig. 4. Fraction of the platinum surface covered with chemisorbed hydrogen atoms ($P_H = 1.94 \cdot 10^{-2}$ mm Hg).

When the observed rate u' of desorption is taken into account, equation (2) assumes the form:

$$\gamma = \frac{\left(C_s - \frac{u' h e^{E'/RT}}{kT}\right) h^2}{2\pi m k T} e^{-E/RT}. \quad (4)$$

Here E' is the activation energy of the process of atom desorption; E is the true activation energy of the recombination process; $u' = K_{\text{desorb}} f'(\theta) e^{-E'/RT}$; K_{desorb} is the rate constant of desorption; $f'(\theta)$ is the fraction of atoms available for desorption.

For the case of nonactivated chemisorption $E' = Q$, where Q is the value of the heat of adsorption, determined in the case of ordinary covalent layers from the difference in bond energies.

To estimate the heat of chemisorption of H atoms on Pt from our experimental data, a very convenient graphical method of calculation according to N. Ya. Buben and A. B. Shekhter⁽¹⁰⁾ was used. Taking into account

for a certain probability of desorption of H atoms, the function

$$N_r = \gamma N = \frac{N e^{-E/RT}}{N + \frac{1}{\tau_0} C_s e^{-E'/RT}} N$$

is maximal at $T = T_{\text{max}}$, when

$$\ln \frac{EN\tau_0}{C_s} + \frac{Q}{RT_{\text{max}}} = \ln(Q - E); \quad (5)$$

N_g is the number of atoms striking 1 cm² of the surface in 1 sec (readily calculated on the basis of the classical kinetic theory of gases); $\tau_0 = 10^{-13}$ sec is the period of oscillation of an adsorbed atom in a direction perpendicular to the surface⁽¹¹⁾.

Fig. 4. Fraction of the platinum surface covered with chemisorbed hydrogen atoms ($P_H = 1.94 \cdot 10^{-2}$ mm Hg).

For a partial pressure of hydrogen $P_H = 1.94 \cdot 10^{-2}$ mm ($T_{\max} = 580^\circ$), the value of the heat of chemisorption obtained by us is 42500 cal/mol (Fig. 3) and is in satisfactory agreement with the value $Q = 36900$ cal/mol, calculated from Pauling's equation for single-bond energies.

In accordance with equation (4), a differential approach to the graph [Fig. 1] is necessary from the point of view of individual temperature intervals of the dependence presented. With increasing temperature and increasing desorption rate, a tendency is seen toward a decrease in the number of active reaction centers C_s . As a result of such separation of the experimental temperature intervals of curves analogous to Fig. 1, it proved possible to carry out approximate calculations of the fraction of the platinum surface $1 - f'(\theta)$ covered with chemisorbed hydrogen atoms at various temperatures (Fig. 4), corresponding to the desorption-rate constants of H atoms from Pt $K_{\text{desorb}} = (4.6-6.3) \cdot 10^{28}$ cm⁻² · sec⁻¹, and also of the mean lifetime τ of a chemisorbed atom on the adsorbent surface (^{11,12}).

The processing of experimental data carried out in this way according to equation (4) is very useful for a more detailed consideration of the mechanism of heterogeneous recombination of atomic gases on solid surfaces.

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