Physical Chemistry

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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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On the Elementary Stages of the Process of Recombination of Hydrogen Atoms on an Aluminum Surface. The Heat of Adsorption of Atoms

Chemisorption of atomic gases is one of the elementary stages of the catalytic recombination reaction, while desorption of atoms can exert—at sufficiently high temperatures—a definite influence on the overall rate of the process. Therefore, in each particular case it is necessary to calculate the corresponding values of the heats Q of chemisorption. Despite its exceptional importance, the calculation of Q for reactions of atomic gases on metal surfaces has been carried out only in a limited number of studies in this field ($^{1-3}$). We have for the first time investigated the influence of the kinetic conditions accompanying heterogeneous recombination reactions—the partial pressure of the atomic gas and the temperature of the catalyst—on the value of Q.

The method of investigation, the reaction conditions, the gas parameters, and the composition of the Al catalyst are described in (^{4}).

Fig. 1. Calculation of the heat of adsorption at values of P_{H}:
1—$7.0 \cdot 10^{-3}$; 2—$1.14 \cdot 10^{-2}$; 3—$1.94 \cdot 10^{-2}$; 4—$3.5 \cdot 10^{-2}$ and 5—$4.69 \cdot 10^{-2}$ mm Hg.

As can be seen from Fig. 1, with increasing partial pressure of H atoms in the system, in connection with the increase in the maximum desorption temperature $T_{\max}$ and the decrease in the mean number C_S of atoms bound to the surface, the graphically calculated values of the apparent heats Q of hydrogen chemisorption on aluminum increase (from 21.5 to 31.0 kcal/mole). Q as a function of pressure is shown in Fig. 2. The decrease in Q at low P_{H} causes a considerable lowering of the activation barrier for desorption.

A chemisorbed atom remains on the Al surface until, through fluctuations of thermal motion, it acquires energy sufficient to overcome the forces holding it. During vibrations of the surface atoms and adsorbed atoms, a continuous exchange of energy occurs through collisions. If at some instant an impulse is imparted to the atom whose component perpendicular to the surface is so large that the corresponding energy exceeds the adsorption energy, then the

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

hydrogen atom will leave the surface. As a result of a decrease in the value of Q, the rate of desorption increases and the overall rate of recombination decreases. The coverage of the Al surface by adsorbed atoms decreases with increasing temperature of the wire and decreasing partial pressure of the gas. At the same time, the values of the apparent heats of chemisorption calculated according to the Schachterschneider method (^{1}) decrease ($\Delta Q \simeq 3$ kcal/mole when the catalyst temperature is raised to 350°).

Naturally, in addition to fluctuations caused by thermal motion, there exist structural fluctuations of the adsorption energy on the surface of the metal. These fluctuations are associated with a definite order in the arrangement of surface atoms; they are much larger in magnitude and play a more important role than fluctuations caused by thermal motion. The metal surface exhibits periodic structural fluctuations—a regular alternation of sites with values of Q somewhat greater and somewhat smaller than the mean value. As is known (^{5}), the heat of adsorption on less active regions of the surface may amount to approximately $^2/_3$ of the value of Q on active regions. The structural fluctuations mentioned above in a solid are extremely sensitive to the temperature factor.

Fig. 2. Dependence of Q on the partial pressure of H atoms

Fig. 3 clearly illustrates the dependence of the calculated values of Q for hydrogen on Al on two principal parameters—the gas pressure and the temperature of the metal. It is characteristic here that the bends in the curves shown in Fig. 3 correspond to the respective values of $T_{\max}$ on the experimental curves of the recombination rates—the wire temperature. From the obtained values of Q, it may be assumed that, as P_{H} increases, desorption is also hindered owing to a disturbance of the regularity of the structure of the metal crystal lattice and to a strengthening of the bond of the atoms of the latter with chemisorbed hydrogen. This is expressed, for example, in the displacement of some atoms from their regular positions at lattice sites and their transition into interstices, which are then gradually eliminated by the return of atoms to the original or to new sites. As is seen from Fig. 3, with increasing wire temperature the value of Q decreases and, evidently, the rate of restoration of the regular structure of the Al crystal, its surface, increases. This becomes understandable if one takes into account the low melting point of Al (660°) and, consequently, the extremely low values of the corresponding annealing and recrystallization temperatures.

Fig. 3. Dependence of Q on the temperature of the catalyst for values of P_{H}: 1—$7.0 \cdot 10^{-3}$; 2—$1.14 \cdot 10^{-2}$ and 3—$1.94 \cdot 10^{-2}$ mm Hg.

Fig. 4

Figure 4: Fig. 4

If it is assumed that dislocations (chiefly) and other disturbances of the regularity of the crystal lattice of the metal act as active centers of chemisorption and subsequent recombination of atoms, then in the temperature interval studied (up to 450°) a significant decrease in the dislocation density is quite probable. Since the atoms forming dislocations, as well as the atoms located on the edges or vertices of crystal faces (Al has a face-centered cubic lattice), are characterized by a higher energy in comparison with "ordinary" atoms, and since the energy of dislocations is very large, a decrease in the density of all these defects appreciably lowers the magnitude of the corresponding heats of adsorption. In accordance with Frenkel (^{6}), the attenuation of dislocations during their motion occurs the more rapidly, the higher the temperature of the body, so that when the latter is heated the average length of dislocations in it decreases and the processes of plastic deformation increasingly degenerate into processes of self-diffusion and recrystallization.

As is known (^{7}), many features of dynamic equilibrium on the surface of an adsorbent depend on the duration of adsorption. In this case, if the adsorption time is sufficiently long, then a complete exchange of thermal energy takes place between the adsorbed particles. As the partial pressure of H atoms in the system increases, the probability of acquiring the activation energy necessary for the desorption process, proportional to $e^{-Q/RT}$, decreases appreciably. At the same time, the mean lifetime τ of the chemisorbed atom increases. The values of τ for H atoms on the surface of aluminum, calculated from the experimental data in the range $P_H = 0.005$–0.05 mm Hg and $t = 20$–$450°$, are presented in Fig. 4. For a given value of P_H, as the temperature of the wire is increased, the mean time interval between adsorption of the particle and its desorption decreases appreciably. The experimental data obtained satisfy the Frenkel equation

$$\tau = \tau_0 \exp(Q/RT). \tag{1}$$

Fig. 4. Temperature dependence of the mean lifetimes τ of chemisorbed hydrogen atoms at values of P_H: 1–$7.0 \cdot 10^{-3}$; 2–$1.14 \cdot 10^{-2}$; 3–$1.94 \cdot 10^{-2}$; 4–$3.5 \cdot 10^{-2}$ and 5–$4.69 \cdot 10^{-2}$ mm Hg.

In this case the pre-exponential factor is also inversely proportional to temperature. Such an influence of temperature is easily explained, since the quantity τ_0 increases with an increase in the number of degrees of freedom retained by the particle during adsorption. The chemisorbed H atoms participating in the elementary act of recombination at lower temperatures of the Al wire are characterized by greater mobility and larger values of the residence time on its surface.

Thus, for the metal catalyzing the recombination reaction of atomic hydrogen (Al), the adsorption energy Q and the time τ are not constant over the whole surface. As a result, desorption occurs primarily at those places on the surface where the attraction is smallest and where the heat of adsorption has the smallest value. These data agree with Roginskii' s theoretical concepts (^{5}) concerning adsorption and catalysis phenomena on heterogeneous surfaces.

The activation energy of the process of atom desorption is a link in the adsorption-catalytic scheme of heterogeneous recombination adopted by us. We next consider whether the calculated values of the heats Q of chemisorption can also serve as a certain, albeit approximate, measure for estimating the corresponding activation energies E of the reaction. Correlations of this kind are known. In particular, an equation relating the quantities E and Q was derived by Shekhter (equation (1) of paper (^{2})) under the assumption that adsorption of atoms follows the Langmuir isotherm. For a more general case, Hirschfelder (^{8}) showed that the activation energy of any exothermic reaction of the type $A + BC \to AB + C$ is approximately estimated by the equation

$$E \cong 0.055\, D_{\mathrm{BC}}, \tag{2}$$

where D_{BC} is the dissociation energy of the molecule BC.

If this semiempirical equation is applied to the exothermic process of heterogeneous recombination of atoms on a clean metal surface, proceeding according to the mechanism $\mathrm{H} + \mathrm{MeH} \to \mathrm{H}_2 + \mathrm{Me}$, then the activation energy

$$E \cong 0.55 D_{\mathrm{MeH}} \cong 0.055\, Q. \tag{3}$$

A more accurate estimate of the value of E from the values of the heat of adsorption of an atom on the surface could be obtained under the condition of the possibil-

the necessity of an exact calculation of the total free energy F of the crystal lattice of the solid (calculated per 1 mole).

Since, as a result of the decomposition of the activated complex MeHH, the energy of its formation is redistributed in the form of the association energy of two atoms into an H_2 molecule and the energy of formation of the metal crystal lattice ($\mathrm{MeHH} \to \mathrm{H}_2 + \mathrm{Me}$, see also Fig. 4 of work (^{4})), then

$$Q - E = E_{\mathrm{H}_2} - F_{\mathrm{Me}}, \tag{4}$$

where E_{H_2} is the dissociation energy of the hydrogen molecule (per 1 mole). Taking as an approximation the Einstein model (^{9}), in which the particles in a simple lattice perform oscillations independently of one another, with the same frequency ν_0, and each does so isotropically about its mean position, we obtain

$$E = Q - E_{\mathrm{H}_2} + N\left\{u(\nu) + 3nkT\left[\frac{1}{2}\xi + \frac{\xi}{e^{\xi}-1}\right]_{\xi=\frac{\theta_D}{0.75\,T}}\right\}. \tag{5}$$

Here $u(\nu) = \dfrac{U}{N}$, where U is the energy of the static lattice, in which each of its particles occupies its mean position; N is the number of cells in 1 mole; n is the number of particles in each cell, and θ_D is the characteristic Debye temperature.

Thus, the rate of heterogeneous recombination of atomic gases is determined by the ratio of the heights of the energy barriers for the formation of the transition state (E) and for the desorption of chemisorbed atoms ($E' = Q$). The latter, in turn, are a very complicated function of a number of parameters that connect the quantities E and E' into a single equation. Being one of the simplest examples of reactions proceeding with the participation of adsorbed atoms, the recombination process from this point of view is of general interest for the theory of heterogeneous catalysis.

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