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Abstract

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Adsorption of Vapors on the Surface of Gold

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In connection with the very interesting results obtained in the study of the adsorption of vapors on the surface of mercury (^{1,2}), we made an attempt to investigate the adsorption of water vapor on the surface of a metal, for example gold. The starting material was a gold plate with a purity of 99.99%, which we rolled on steel rolls to a thickness of 7.8 μ. Separate sheets of this foil were fastened together with gold wire in the form of a booklet. The oil that had gotten onto the foil during rolling was removed by extraction with benzene in a Soxhlet apparatus. After this the sample was treated with hydrochloric and nitric acids to remove possible contamination by the steel of the rolls.

For measuring adsorption isotherms, the Bering and Serpinskii adsorption balances (^{3}) were used; their sensitivity for the present investigations was increased to $5.2 \cdot 10^{-8}$ g at a load of 1 g. The necessity of this was due to the fact that the foil we prepared, with a weight of 1.09 g, had a geometrical surface of only 143 cm^2. The increase in sensitivity was achieved by a better balancing beam, which naturally led to a narrowing of the permissible weighing range to 1 mg.

The manometric part of the apparatus was also modified, since in studying the adsorption of water vapor it became impossible to freeze out mercury vapor. Therefore the mercury manometers were replaced, for low pressures (from 10^{-5} to 0.1 mm Hg), by a Pirani-type manometer, and for medium pressures (from 0.01 to 30 mm Hg and higher) by a membrane manometer. The Pirani manometer was made of platinum wire 30 μ in diameter and 10 cm long, stretched in a glass tube with an internal diameter of 4 mm. The latter was surrounded by a buffer water jacket, through which passed a glass coil with circulating water from a TS-15 thermostat. The temperature of the filament was kept constant (100°) by varying the current feeding a Wheatstone bridge, one arm of which was the filament. The bridge current necessary for maintaining a constant temperature, and consequently a constant resistance of the filament, which is a function of the pressure, was measured with a PN-4 potentiometer. The membrane manometer was made of glass with a membrane 30 mm in diameter; its deformation was measured by means of a mechanical system with a mirror and an autocollimation tube. Both manometers were placed in the air thermostat of the balances.

The very first experiments with this adsorbent showed that the electrostatic

Fig. 1

Figure 1: Fig. 1

charges accumulating on the metallic screens of the balances and on the gold foil suspended from a quartz hanger were not removed to the necessary extent by the external electrostatic screen that had been used in the first works (previously the screen had been grounded aluminum foil, with which the outside of the balance casing was wrapped). The introduction of radioactive preparations into the balance casing not only did not reduce the electrostatic "interference," but caused still greater electrification, which manifested itself in the form of individual sparks of electric discharges inside the casing. In this connection the inner cavity of the balance casing in the region of the adsorbent and all the actual balance parts had to be coated with a layer of gold condensed in vacuum and grounded. Only after this did the balances begin to give stable, reproducible readings.

To remove substances that the gold had absorbed from the air and during processing, the specimen under study was heated in vacuum on the balance at a temperature of 420–450°. A loss of weight was observed over 4–5 days; then, over the following 2–3 days, the weight did not change.

The adsorption isotherm of water vapor at 18° that we obtained is shown in Fig. 1. In adsorption experiments at relative pressures from 0 to $0.8\,P/P_s$, a rapid, practically instantaneous course of the process was observed (curve 1), followed by a slow (20–30 hr) increase in the weight of the adsorbent until equilibrium was established (curve 2). The graph shows the results of three independent series of measurements. In desorption experiments from relative pressures of 0.8 and lower, the desorption points fall on curve 2. As is seen from the graph, curve 2 does not pass through the origin, i.e., prolonged (up to 10 days) pumping of gold at 18° does not remove the substance absorbed by it. Subsequent adsorption and desorption points consistently fall on curve 2. Thus, it may be concluded that the rapid initial physical adsorption of water vapor on the surface of gold is accompanied by chemical adsorption. Naturally, curve 1 cannot be regarded as a curve of physical equilibrium adsorption, since, despite the rapid conduct of the experiment, with successive admissions of water vapor, in addition to equilibrium physical adsorption, chemical absorption also partially occurs.

Fig. 1. Isotherm of sorption of water vapor on the surface of gold at 18°: **1** –adsorption, **2** –desorption

The kinetic curve of this process is shown in Fig. 2. Unfortunately, an attempt to calculate the activation energy from the kinetic curves was not successful, because with such a small surface area of the adsorbent the accuracy of the measurements proved insufficient for such calculations.

Fig. 2. Kinetics of absorption of water vapor by gold at 18°. Relative pressure $\sim 0.4\,P/P_s$

Fig. 2

Figure 2: Fig. 2

Fig. 3. Adsorption of benzene vapor on the surface of gold at 18°

Figure 3: Fig. 3. Adsorption of benzene vapor on the surface of gold at 18°

Complete removal of the absorbed substances occurs in vacuum upon prolonged holding of the gold at a temperature of 420–450° (30–40 hours). Repeated investigations after removal of the absorbed substances completely reproduced the picture described.

In order to make sure that the irreversibility we obtained was not connected with the absorption by gold of mercury vapor, vacuum grease, or any other contaminants accidentally entering the apparatus, a control experiment with nitrogen was carried out. After complete removal of the absorbed substances by heating, dry nitrogen was admitted into the balance (to a pressure of 4 mm Hg). During 15 days no increase in the weight of the gold was observed.

Then the nitrogen was replaced by oxygen (at a pressure of 4 mm Hg); in this case, over the course of a day, the gold increased slightly in weight (not more than 0.01 μM/g). The oxygen was then pumped out without heating (the weight of the specimen did not change), and water vapor was admitted into the balance (to a pressure of 4 mm Hg). The point obtained at once lay midway between curves 1 and 2, and after 2 hours the points shifted to curve 2, and during a day of further noticeable change

no weight change occurred. After this, the adsorption and desorption points fell steadily on curve 2. Thus one may conclude: water vapor is chemically adsorbed by gold, probably with the formation of surface oxides or hydroxides. Preliminary chemical adsorption of oxygen accelerates this process.

For quantitative calculations we were interested in the actual surface area of the specimen under study. For this purpose an attempt was made to measure the adsorption isotherm of nitrogen vapor at its boiling point. However, the adsorption quantities were too small and were obscured by convective currents inside the balance, since it proved impossible to eliminate them completely. Therefore, in order to calculate the specific surface area, the adsorption isotherm of benzene vapor was measured (Fig. 3). This isotherm is well described by the Brunauer, Emmett, and Teller equation in the range 0.02—0.35 P/P_s. Applying this equation and taking the area occupied by a benzene molecule in a continuous monomolecular adsorbed layer as 45 Å^2 (the average value, according to A. V. Kiselev, for the adsorption of benzene on carbon black (4)), we obtained a specific surface area of gold of $s = 180$ cm^2. Thus the roughness coefficient was about 1.4. This agrees well with the data of Bowers (5), who found a roughness coefficient of 1.3 for aluminum foil.

Fig. 3. Adsorption of benzene vapor on the surface of gold at 18°

The convex character of the primary adsorption isotherm (curve 1) indicates that we are dealing with adsorption of the electrostatic type under the action of image forces. The entire surface of the adsorbent is active with respect to adsorption.

After desorption at 18°, about 0.155 $\mu M/\text{g}$ of water remains on the adsorbent (irreversibly retained). If one assumes that this amount of water covers the gold surface with a monomolecular layer, then, using the specific surface area we found, one obtains that each water molecule occupies an area of 17 Å^2 on the gold surface. This value differs appreciably from the accepted value of 14.8 Å^2 and from the data of Harkins and Jura, 13.8 Å^2 (^{6}); however, it agrees very well with the area occupied by each gold atom on its surface (16.55 Å^2). Consequently, within the limits of experimental error, one molecule of strongly bound water corresponds to each gold atom on its surface, and the area occupied by a water molecule on the gold surface is determined not only by the dimensions of the water molecule itself, but also by the parameters of the crystal lattice.

At present we are carrying out work to refine these data and increase the accuracy of the investigation, since with the existing method the accuracy of the measurements is not sufficient. This is evident at least from the fact that the entire effect of adsorption of water vapor on our specimen at $P/P_s = 0.5$, equal to $5.7 \cdot 10^{-6}$ g, is measured, in the best case, with an accuracy of 50%.

In conclusion I express my deep gratitude to Academician M. M. Dubinin and V. M. Lukyanovich for their constant attention and valuable advice, and to N. N. Moskvitin for assistance rendered in carrying out several lengthy measurements.

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