Reports of the Academy of Sciences of the USSR

CHEMISTRY

1962

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1962, Vol. 142, No. 5

CHEMISTRY

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PHYSICAL STUDY OF THE YELLOW AND RED FORMS OF MERCURIC OXIDE

For a number of metallic oxides, different colors are characteristic when they are obtained by different methods, although the crystalline structure of the oxide remains one and the same. A striking example of this class of compounds is mercuric oxide, with its well-known red and yellow forms. This difference in color between the two forms has long remained a subject of discussion, and although unequal particle sizes are usually accepted as the self-evident cause ([1]), to our knowledge there is no convincing experimental evidence in favor of this point of view. Likewise, this question is not discussed in the light of modern theories of the solid state. We have carried out a series of experimental studies, the aim of which was to examine in detail the indicated approach to the question and also to take into account other possible factors influencing the change in color. The results obtained are presented here briefly. These investigations are still being continued by us.

Particle-size measurements

a. Sedimentation method. Suspensions with particles of different sizes were obtained by passing nitrogen bubbles through oxide samples under identical conditions until stable suspensions were produced. When the Svedberg-Oden method ([2]) was applied using a Wiegner column ([3]), statistical treatment of the results according to Tessner ([4]) led to the most probable values of the particle radius: $14.9\,\mu$ for red mercuric oxide and $13.6\,\mu$ for yellow. Although the numbers obtained are very close, these results do not exclude the possibility that the particles of the yellow oxide consist of smaller particles cemented into larger ones by secondary forces.

b. Powder X-ray diffraction method. For both forms of the oxide, a series of powder X-ray diffraction patterns was obtained in cameras 9 and 19 cm in diameter. In practice, no difference between the two forms could be established either in the interplanar spacings or in the relative total (integral) intensities. This shows that the crystalline structure of both forms is the same. The only observed difference was the broadening of some diffraction lines in the yellow form. Such broadening may be due to one of the following causes.

1. Particle sizes. The broadening $\delta\theta$ is related to the dimensions of the crystallites by the relation

$$t = \frac{m\lambda}{\cos\theta\,\delta\theta},$$

where t is the average thickness of the crystallites of which the powder consists, θ is the Bragg angle, λ is the wavelength of K_α, and m is a constant.

2. Microstresses. They are determined from the ratio of the change in the Bragg interplanar spacing for a certain reflection to the initial value of this spacing for the same reflection:

$$\frac{\delta d}{d} = \frac{\delta\theta}{\operatorname{tg}\theta}.$$

3. Thermal vibrations. The broadening produced by thermal vibrations of atoms in a crystalline solid, which is reflected in the "shoulder" width of the peaks (^{5}), can be eliminated by comparing the same reflection (hkl) for both forms, using radiations of different wavelengths. If the broadening is entirely determined by the particle sizes, then there must be a direct proportionality between $\delta\theta$ and λ. On the basis of these considerations, we obtained radiographs with different radiations (K_α-lines from Mo, Cu, Co, and Cr anticathodes). Recording was carried out with a diffractometer. From the observed line widths we find the true peak broadening by Warren' s method, which is based on taking into account the line broadening produced by the slit system, as well as by the combined participation of the K_α- and K_β-lines in the reflection. Analysis of the X-ray diffraction data corrected in this way showed that:

(a) There is no direct proportionality between $\delta\theta$ and λ, and therefore X-ray diffraction does not make it possible to determine the mean particle sizes, since in this case different results will be obtained for one and the same powder depending on the radiation with which the photograph was taken.

(b) The microstresses in the yellow form are more pronounced than in the red. These stresses are produced either by defects in the lattice or are associated with centers in which impurities are concentrated (^{6}).

Dielectric constant

Dry samples were successively placed in one and the same capacitor, with identical packing conditions and temperature maintained. Using Böttcher' s formula (^{7}), we obtained values for the dielectric constant of 12.6 for the red form and 9.4 for the yellow form at 100 kHz and a temperature of 25°, with porosity also taken into account. Further experiments made it possible to cover the interval from 50 kHz to 5 MHz at different temperatures. Measurements of dielectric losses at low temperatures, which we regard as preliminary, showed that both forms of HgO contain centers with impurities, which in the red form are ionized more easily than in the yellow. Further, at temperatures below approximately −25°, recombination occurs in the red form with a change in color to yellow. On the other hand, when the yellow form is heated to a temperature above room temperature, substantial ionization occurs in it and it turns red.

Temperature dependence of conductivity

We measured relative values of conductivity at different temperatures in the interval from 100 to 250° C in order to calculate the activation energy for both forms from the equation $\sigma_T = \sigma_0 e^{-E/kT}$, where σ_T is the conductivity at a certain temperature T, σ_0 is the conductivity at infinitely high temperatures, and E is the difference between the values of the electrical conductivity at the boundaries of the interval in which the measurements were made. All measurements were carried out using a specially constructed cell with two electrodes. The frequency interval was from 50 Hz to 40 kHz at 25 V and in the temperature intervals 373–523° K and 373–473° K. The averaged values found for the energy differences for the indicated intervals were 1.18 eV for the red form and 1.02 eV for the yellow form. The results of the electrical-conductivity measurements make it possible to conclude that the formation of charge carriers in yellow mercury oxide occurs somewhat more energetically than in the red form in the indicated temperature intervals.

Magnetic susceptibility

The mean values of the magnetic susceptibility for the two forms were determined by Gouy' s method in a magnetic field of 7000 G. The values obtained at 25° ···

the values were $-0.221 \cdot 10^{-6}$ and $-0.216 \cdot 10^{-6}$ emu/g, respectively, for the yellow and red forms. The dependence of the susceptibility on temperature was studied in the interval 25—266°C. These measurements have not been completed, and we propose to extend their range toward low temperatures. Apparently, the temperature behavior of the diamagnetic susceptibility is associated with the presence of impurities capable of ionization.

On the basis of the measurements carried out, it may be supposed that in both forms of mercuric oxide there are centers with impurities which, normally, in the red form are ionized more energetically than in the yellow. This may help to explain the higher values of the dielectric constant at room temperature and is in agreement with all the described measurements of the physical constants.

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Received10 XI 1961

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