THE EFFECT OF GELATINE ON THE POLYMORPHIC TRANSFORMATION OF MERCURIC IODIDE.

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The author studied the effect of various colloidal substances on the formation of mercuric iodide from mercuric chloride and potassium iodide solutions.[1] In the present note the effects of gelatine on the transition between red and yellow modifications of mercuric iodide are described.

The mercuric iodide was prepared from the equivalent quantities of the solutions of mercuric chloride and potassium iodide, and then it was washed with water and dried. About 0.5 gram of gelatine was dissolved in a few cubic centimetre of hot water and added about 20 grams of mercuric iodide, mixed them well by grinding in a mortar. The viscid red mass thus produced was spread on a glass plate, which had previously been coated with a thin film of paraffin in order to prevent the sticking of gelatine on the surface of glass when dried. After the mass was dried, it was taken off the glass plate, and a few of the small pieces was put in a glass capillary tube.

The pure mercuric iodide powder was put in a capillary tube of the same dimensions as above. These two tubes, the one containing the gelatinized mass and the other the pure mercuric iodide, were put in a bath of the heating liquid ("liquid paraffin" was used) side by side providing a thermometer and a stirrer. Then the liquid was heated and the colour changes of the two tubes were observed.

The heating rate was about one degree per five minutes. At 125–130°C. the colour of the pure mercuric iodide began to turn yellowish, and at 132°C. it changed to yellow completely. The gelatinized mercuric iodide, however, showed no sign of colour change at this temperature and remained in red. The gelatinized one began to change its colour at about 150°C. and it turned more and more yellowish by the elevation of the temperature. At so high a temperature as 168°C. the colours of the two capillary tubes became identical.

Now the burner was turned off and the bath was left to cool. At a temperature lower than 127°C. there appeared some red spots in the pure mercuric iodide tube, and increased their areas by and by, which at last, after a few minutes, spreaded all over the mass of iodide and turned completely to red form. Yet, the gelatinized one retains its yellow colour

(1) Sameshima and Suzuki, this journal, 1 (1926), 81.

even after cooled down to the ordinary room temperature. After some times, the surface of the gelatinized yellow mass is contaminated with some red powder, which is small crystals of mercuric iodide sublimed out onto the surface from the gelatinized mass. Therefore, if the mass is taken out from the tube and broken, it can be seen that the inside of it is quite yellow. The inside of the gelatinized mass remains yellow for months after the time of heating. Thus the yellow form may remain unchange at ordinary tempera ture for indefinite length of time. But if we scratch the yellow part with something like a pencil knife the part immediately turns to red.

The above described phenomena may be interpreted as follows. In the present case, gelatine act as a protecting colloid in solid phase. It retards the velocities of transformations between red and yellow mercuric iodide, over and under their transition temperature 127°C. It is a general fact that, in a mean time, there may take appearance a few number of nuclei of the stable phase out of the supercooled or superheated phase. These nuclei, then, grow in their size and at last all of the mass changes to the stable phase. But if there exist the gelatine or other colloidal substances and each particles of the supercooled or superheated phase are enveloped by these colloid, then the growing of the nuclei will be hindered, even though they appeared here and there. We may say, in general, that the transition point between enantiotropic modifications will be made unsharp by the presence of the colloidal impurities, or shows hysteresis in the transition temperature. In the other hand, these phenomena may throw some light on the Smits' theory of allotropic modifications.

An interesting lecture demonstration can be performed in the following manner. One gram of gelatine is dissolved in 10 c.c. of hot water, and the solution is transferred into a mortar, add 20 grams of mercuric iodide and mix thoroughly by grinding with a pestle. The red viscid mass thus obtained is then spread by a brush on a clean glass plate to a thin layer, and dried by gently warming on a water bath. Now half a gram of gelatine is dissolved in 5 c.c. of hot water and paint it over the red coating above described. The latter treatment is necessary because it prevent the deposition of the sublimed mercuric iodide crystals on the surface of the gelatinized layer. After drying, the plate is put in an air bath and uniformly heated to about 170° C. in a draught chamber. When the plate turns to yellow completely, it is taken out from the bath and left to cool.

The yellow plate thus obtained will retains its colour for indefinite length of time. It is the protected supercooled yellow modification of mercuric iodide. Now the plate is brought before the audience, and scratch the yellow mass with the finger nail or a pencil knife. The scratched portion will immediately changes its colour to red, while the untouched

portion will remain in yellow. We can write, therefore, some letters or figures in red colour on the yellow surface.

Moreover, an interesting fact was observed. On heating the gelatinized red iodide on a desk near the window, the lighter side of the mass turns yellow first and then the darker side follows it afterward. On keeping the yellow mass near a window at the ordinary temperature, the light side of the surface contaminated firstly with the red powder of sublimed iodide, while the dark side remains yellow longer. Thus the light energy accelerate the transformation velocity of the polymorphic changes.

Summary.

The mercuric iodide containing gelatine shows hysteresis on the transition temperature, i.e. it is necessary to heat considerably higher than 127°C. to transform the red modification into the yellow one, and on the contrary, the yellow one remains unchange for indefinite length of time at the room temperature. In this case gelatine act as a protecting colloid in a solid phase.

A lecture demonstration has been described of showing the behavior of the protected suppercooled mercuric iodide.

The transformation of mercuric iodide of metastable form to that of stable one is accelerated by the light energy.

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