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On the Stability Relations and Solubilities of Hexagonal and Orthorhombic Mercury(II)oxide

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The hexagonal modification of mercury(II)oxide is found to be metastable with regard to the orthorhombic oxide, from at least room temperature and up to the decomposition temperature, from experiments transforming the hexagonal oxide into the orthorhombic modification and from solubility measurements in water.

The solubility obtained for the hexagonal modification is 2.55×10^{-4} mole/l at 25°C. For the transition HgO(hexagonal) = HgO (orthorhombic, red) at 25°C an approximate value is calculated for the Gibbs energy change, $\Delta G = -72 \pm 10$ cal/mole. Approximate values of ΔH and ΔS were determined: $\Delta H = -300 \pm 200$ cal/mole, $\Delta S = -1 \pm 1$ cal/mole · degree.

In connection with studies of the crystal structures of orthorhombic and hexagonal mercury(II)oxide [1,2], it seemed of interest to study the stability relations between these different modifications. The relationship between the red and yellow modifications of the orthorhombic oxide has been studied earlier by several methods [3–7] which seemed to indicate that the two oxides were identical, the discrepancies in colour and solubility being due to a difference in particle size.

PREPARATIONS AND ANALYSES

The hexagonal mercury(II)oxide was synthesized by mixing one part of 0.1 M K_2HgI_4, containing an excess of 0.025 M KI, with two parts of 5.5 M NaOH at about 50°C (Ref.[2]). After a few hours the resulting precipitate was decanted and washed with hot water. In spite of numerous experiments, no other method of preparation has been devised.

Red mercury(II) oxide was prepared by ignition of the pure nitrate on a sand bath until it was completely decomposed, and the resulting product was then carefully washed. The mercury(II)nitrate was prepared by dissolving redistilled reagent quality mercury in nitric acid, *pro analysi*, and partially crystallizing the solution.

Commercial yellow mercury(II)oxide, *e.g.* reagent quality from J. T. Baker, Phillipsburg, N. J., was found to give reproducible solubilities in agreement with values found by previous authors and was therefore used in the experiments.

All samples of the mercury(II)oxides (checked for purity by means of amply exposed X-ray powder photographs) were agitated for several weeks in conductivity water that was frequently changed. This washing procedure was done to eliminate the finest particles and to remove possible traces of impurities that were not discovered in the powder diagrams.

Table 1. Hydrothermal heating of hexagonal HgO in 5 M NaOH at different temperatures.

Temperature °C	Time of heating	Resulting phases in the sample
		5 M NaOH
200	2 days	HgO_{rh}, HgO_{hex}
170	2 days	HgO_{rh}, HgO_{hex}
130	2 days	HgO_{rh}, HgO_{hex}
100	2 days	HgO_{hex}, HgO_{rh}
60	6 weeks	HgO_{hex}, HgO_{rh}
35	8 weeks	HgO_{hex}, HgO_{rh}
25	8 weeks	HgO_{hex}

The analyses of mercury were carried out by titrating Hg(II) with a standard solution of KSCN using Fe(III) as an indicator (principally according to Kolthoff and Sandell[8]) or by potentiometric titration[7] with a standard solution of KI. The thiocyanate method is considerably quicker than the potentiometric one but does not give the same precision, the reproducibilities being estimated to be 0.8 and 0.2 % respectively. The results of the thiocyanate titration and of the potentiometric method were found to agree within the limits of experimental error.

THE STABILITY RELATIONS OF HEXAGONAL AND ORTHORHOMBIC MERCURY(II)OXIDE

By heating the hexagonal oxide to temperatures above 200°C, Laruelle[9] was able to convert it into the orthorhombic modification. We also obtained the same result above 200°C and have furthermore succeeded in performing the conversion at temperatures down to 35°C. However, the fact that the reaction velocity of the transition decreases greatly with decreasing temperature made it necessary to use another method than the dry heating of the samples. We were able to perform the conversion within a reasonable time by means of hydrothermal heating. A small amount of pure hexagonal oxide in a gold tube was sealed off in a thick walled glass tube together with a quantity of 5 M NaOH. At temperatures above 100°C, the samples were kept in

Table 2. Solubilities of red and yellow orthorhombic HgO in water at 25°C. The solubilities are given in 10^{-4} mole/l.

Investigator	Ref.	Year	Red HgO	Yellow HgO
Ostwald, W.	3	1900		2.41
Hulett, G. A.	10	1901	2.34	
Schick, K.	11	1903	2.37	2.39
Fuseya, G.	12	1920	2.33	
Garrett, A. B. and Hirschler, A.E.	7	1938	2.25	2.37
Ragg, M.	13	1950	2.88	2.92
Bruja, N. Z.	14	1954	2.52	4.20

an electric oven while, below this temperature, the samples were agitated in a thermostat. After cooling, the samples were washed and X-ray powder photographs were taken. At all temperatures from 35 to 200°C, proof was obtained of a partial conversion of the hexagonal oxide into the orthorhombic modification (Table 1). In this table, the predominant component is the first mentioned one. Later on (Table 6), it was shown by experiments that the hexagonal modification is more soluble than the orthorhombic ones down to at least 25°C.

Since an estimation of the particle sizes of some samples (Table 5) indicates that the finest particles of the hexagonal oxide are of a size somewhere between those of the two orthorhombic modifications, the differences in the particle sizes cannot be the reason for the higher solubility of the hexagonal oxide.

Thus, from these experiments, the conclusion can be drawn that the hexagonal mercury(II)oxide is metastable with regard to the orthorhombic modifications from room temperature up to the decomposition temperature (~ 500°C).

THE SOLUBILITY OF HEXAGONAL AND ORTHORHOMBIC MERCURY(II)OXIDE

The solubility values at 25°C of the red and yellow modifications of orthorhombic HgO found in the literature are given in Table 2.

To check our experiments, we at first redetermined the solubilities of the orthorhombic modifications of HgO at 25°C and obtained 2.26×10^{-4} and 2.36×10^{-4} mole/l, respectively, practically the same values as those found by the other authors with the exception of Ragg and Bruja.

EXPERIMENTAL

The samples, 0.1—2 g oxide and about 100 ml conductivity water, were sealed in glass flasks and rotated in a water thermostat at 25.00° and 35.00°C or in an air thermostat at 50.0° and 60.0°C. The accuracy of the water thermostat was ± 0.03° and of the air thermostat ± 0.1°. A preliminary study of the reaction velocity indicated that the mercury(II) oxide attained its equilibrium solubility in water at 25°C within a few days but the samples were always rotated for two to four weeks. At higher temperatures a shorter time was used.

The flasks were opened and placed in a metal vessel at the proper temperature. The solutions were filtered by nitrogen pressure through sintered glass filters of porosity G4 and analysed for Hg(II).

Table 3. The solubilities (in 10^{-4} mole/l) of different samples of red orthorhombic HgO in water at 25°C. The experiment was repeated for each sample up to three times. The mean value is $(2.26 \pm 0.03) \times 10^{-4}$ mole/l with 95 % confidence.

Run	Sample				
	a	b	c	d	e
1	2.24	2.25			
2	2.26	2.22	2.29	2.23	2.35
3	2.24	2.22	2.27	2.26	2.31

Table 4. The solubilities (in 10^{-4} mole/l) of yellow orthorhombic HgO in water at 25°C, the equilibrium being approached from both undersaturation and supersaturation. The mean value is $(2.36 \pm 0.03) \times 10^{-4}$ mole/l with 95 % confidence.

From undersaturation			From supersaturation		
2.28	2.30	2.36	2.32	2.34	2.37
2.38	2.40	2.41	2.38	2.39	2.39
	2.36			2.37	

Table 5. Estimated particle sizes of some samples of HgO at a magnification of 800 times.

Sample	Particle diameter (μ)		
	Main body of the sample	Smallest observed	Value given by Garrett and Hirschler
Hexagonal HgO	5—35	~0.5	—
Yellow orthorhombic HgO	0.5—14	<0.5	<0.5—10
Red orthorhombic HgO	10—60	~1.0	10 —30

Table 6. The solubilities (in 10^{-4} mole/l) of the hexagonal, yellow orthorhombic and red orthorhombic modifications of HgO in water at different temperatures. The number of experiments at the different temperatures are given. The errors are reported for 95 % confidence.

Temp. °C	HgO hexagonal	Number of expts.	Yellow HgO orthorhombic	Number of expts.	Red HgO orthorhombic	Number of expts.
60.0	7.75 ± 0.07	10	7.57 ± 0.09	12	7.34 ± 0.09	12
50.0	5.55	5	5.42	5	5.17	5
35.00	3.42	5	3.25	5	3.16	5
25.00	2.55 ± 0.04	18	2.36 ± 0.03	12	2.26 ± 0.03	12

The solubility of the hexagonal modification was often abnormally high in the first few runs, a fact that probably was due to traces of impurities not revealed in the X-ray diagrams. The solubilities of the samples decreased when the impurities were washed out and a constant value was attained.

A check of the X-ray powder pattern of some hexagonal samples used in a great number of experiments revealed their partial conversion into the orthorhombic modification. As the solubility of the hexagonal oxide has been found in this investigation to exceed the solubility of the orthorhombic oxide, this partial transition does not have any importance as long as there is some of the hexagonal oxide left. To get a reliable connection between the solubilities of a modification at different temperatures, most samples were run at all the temperatures investigated. The results of the experiments are given in the following tables. Table 3 gives a survey of a series of experiments with different samples of red orthorhombic HgO at 25.00°C and Table 4 a comparison between measurements of the solubilities of yellow orthorhombic HgO, some of the samples being allowed to approach the equilibrium from undersaturation and the others from supersaturation. Microscopic measurements of some of the samples at a magnification of 800 times led to an estimation of the particle sizes given in Table 5.

Table 6 shows the resulting solubilities of red and yellow orthorhombic HgO and of hexagonal HgO at different temperatures (25.0°—60.0°C). As seen, the hexagonal modification is at all temperatures investigated, the most soluble one. It is also evident that the yellow modification of orthorhombic mercury(II)oxide is more soluble than the red one. This difference in the solubility can of course be considered as depending on the difference in particle size as stated in the literature [7]. By microscopic measurements (Table 5) such a difference in the particle size was also revealed in the present investigation. However, a possible difference in the arrangement of the oxygen atoms in the structures of the two orthorhombic modifications may also give a difference in the solubility. The X-ray powder diffractograms of the red and yellow oxides are identical, indicating the positions of the heavy mercury atoms are the same but giving no knowledge about an eventual difference in the oxygen atom arrangements. Such a difference might be revealed by neutron powder diffractograms of these two modifications. Therefore a neutron diffraction investigation of a powder sample of the yellow modification is being done; the red modification has been investigated by neutron diffraction methods before [1].

THE THERMODYNAMIC FUNCTIONS FOR THE REACTION HgO (HEXAGONAL) = HgO (ORTHORHOMBIC, RED)

According to Garrett and Hirschler [7], Hietanen and Sillén [15] and Dyrssen and Tyrrell [16] the mercury-containing species in the aqueous solution are mononuclear. Accepting this view, a value of the Gibbs energy change, $\Delta G = -72 \pm 10$ cal/mole, can be calculated for the transition HgO (hexagonal) = HgO (orthorhombic, red) from the solubility data at 25.0°C. The values of ΔG calculated for the other temperatures investigated are given in Table 7.

From the solubility values at different temperatures an approximate value of $\Delta H = -300 \pm 200$ cal/mole and of $\Delta S = -1 \pm 1$ cal/mole · degree were estimated, the variation of ΔG with temperature approximated to a straight line. These values are of the same order as those calculated from values given in the literature [17] for the reaction HgO (orthorhombic, yellow) = HgO (orthorhombic, red). A preliminary value of $\Delta H = -0.2 \pm 1.0$ kcal/mole for the transition above was also obtained from calorimetric measurements of the heats of solution in 4 M HCl of hexagonal and of orthorhombic, red mercury(II)oxide. The potential difference between the electrodes

$$\text{Hg,HgO(hexagonal)}|\text{OH}^- \text{ and } \text{Hg,HgO(orthorhombic, red)}|\text{OH}^-$$

Table 7. Calculated values of the Gibbs energy change ΔG for the transition HgO (hexagonal) = HgO (orthorhombic, red) at different temperatures.

Temperature °C	25.00	35.00	50.0	60.0
ΔG cal/mole	−72	−47	−42	−32

was calculated to $e_{\mathrm{hex}} - e_{\mathrm{rh}} = 1.5$ mV from the Gibbs energy change, given above. However, this will not influence the values hitherto measured with the electrode Hg,HgO(orthorhombic, red) | OH^- as there is no proof that orthorhombic mercury(II)oxide synthesized by conventional methods contains any hexagonal mercury(II)oxide.

DISCUSSION

From crystallographic point of view, the hexagonal and orthorhombic modifications of mercury(II)oxide are very much alike. The hexagonal oxide is built up of infinite spiral chains —O—Hg—O— while the orthorhombic one contains infinite planar zig-zag chains —O—Hg—O—. The distances and angles between the mercury and oxygen atoms and the coordination of the atoms are almost the same in both structures. The single crystals of these two modifications show very often an epitaxial growth which could be interpreted as being due to a transition of the infinite spiral chain into the infinite planar zig-zag chain. This structural resemblance suggests that physical properties such as solubility should be nearly the same, which is also supported by the experimental values obtained in this work. There seems, however, from crystallographic point of view to be no obvious reason for the orthorhombic form to be more stable than the hexagonal one which is the unambiguous result from the present investigation.

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REFERENCES

1. Aurivillius, K. *Acta Chem. Scand.* **10** (1956) 852.
2. Aurivillius, K. and Carlsson, I.-B. *Acta Chem. Scand.* **12** (1958) 1297.
3. Ostwald, W. *Z. physik. Chem.* **34** (1900) 495.
4. Cohen, E. *Z. physik. Chem.* **34** (1900) 69.
5. Taylor, G. B. and Hulett, G. A. *J. Phys. Chem.* **17** (1913) 565.
6. Levi, G. R. *Gazz. chim. ital.* **54** (1924) 709.
7. Garrett, A. B. and Hirschler, A. E. *J. Am. Chem. Soc.* **60** (1938) 299.
8. Kolthoff, I. M. and Sandell, E. B. *Textbook of Quantitative Inorganic Analyse*, 3rd Ed. New York 1952, p. 547.
9. Laruelle, P. *Compt. rend.* **241** (1955) 802.
10. Hulett, G. A. *Z. physik. Chem.* **37** (1901) 406.
11. Schick, K. *Z. physik. Chem.* **42** (1903) 172.
12. Fuseya, G. *J. Am. Chem. Soc.* **42** (1920) 369.
13. Ragg, M. *Farbe und Lack* **56** (1950) 435.
14. Bruja, N. Z. *Rev. chim. Bucharest* **5** (1954) 173.
15. Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* **6** (1952) 747.
16. Dyrssen, D. and Tyrrell, V. *Acta Chem. Scand.* **15** (1961) 393.
17. *National Bureau of Standards circular* 500 (1952), p. 199.

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