[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Solubility Relations of Mercuric Oxide in Aqueous Solutions of Hydrogen Chloride[1]

BY A. B. GARRETT AND JAMES LEMLEY

This paper presents data on the solubility of mercuric oxide (yellow) and basic mercuric chloride ($2HgO \cdot HgCl_2$) in dilute solutions of hydrochloric acid. The data on the mercuric oxide–hydrochloric acid equilibria are similar to those obtained in a study of the mercuric oxide–nitric acid equilibria[2] which involve the hydrogen ion effect, but these have the additional interest in that they include the reaction with the chloride ion. Hence, the following equilibria are involved in interpreting the mercuric oxide–hydrochloric acid data in the very dilute range.

$$HgO(s) + H_2O \rightleftarrows Hg(OH)_2(aq.) \quad (1)$$

$$HgO(s) + H^+ \rightleftarrows Hg(OH)^+ \quad (2)$$

$$HgO(s) + 2H^+ \rightleftarrows Hg^{++} + H_2O \quad (3)$$

$$HgO(s) + H^+ + Cl^- \rightleftarrows Hg(OH)Cl(aq.) \quad (4)$$

$$HgO(s) + 2H^+ + 2Cl^- \rightleftarrows HgCl_2(aq.) + H_2O \quad (5)$$

$$HgO(s) + 2H^+ + 3Cl^- \rightleftarrows HgCl_3^- + H_2O \quad (6)$$

$$HgO(s) + 2H^+ + Cl^- \rightleftarrows HgCl^+ + H_2O \quad (7)[3]$$

Since the compound $2HgO \cdot HgCl_2$ was identified as the solid phase in the higher concentrations of acid, the following additional reactions are to be considered

$$3HgO(s) + 2H^+ + 2Cl^- \rightleftarrows 2HgO \cdot HgCl_2(s) + H_2O \quad (8)$$

$$2HgO \cdot HgCl_2(s) + H_2O + H^+ + Cl^- \rightleftarrows 3Hg(OH)Cl \quad (9)$$

$$2HgO \cdot HgCl_2(s) + 4H^+ + 4Cl^- \rightleftarrows 3HgCl_2(aq.) + 2H_2O \quad (10)$$

$$2HgO \cdot HgCl_2(s) + 4H^+ + Cl^- \rightleftarrows 3HgCl^+ + 2H_2O \quad (11)$$

$$2HgO \cdot HgCl_2(s) + 4H^+ + 7Cl^- \rightleftarrows 3HgCl_3^- + 2H_2O \quad (12)$$

The preparation of this trimercuric oxychloride is described in this paper. The existence of it is reported in early work.[4]

(1) Original manuscript received April 5, 1940.

(2) Garrett and Howell, THIS JOURNAL, **61**, 1730 (1939).

(3) Other equilibria may be indicated by writing such equations as

$$HgO + Cl^- \rightleftarrows HgOCl^- \quad (a)$$

$$2HgO + 2Cl^- + H_2O \rightleftarrows 2Hg(OH)Cl \quad (b)$$

However, equations (a) and (b) seem very improbable due to the pronounced hydrogen ion effect in this reaction.[2]

(4) See Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans and Company, London, 1923, Vol. IV, pages 839–844, for a discussion of the oxychlorides of mercury. Reference is given here to several of the early workers who crystallized $2HgO \cdot HgCl_2$ from a hot solution containing mercuric oxide and mercuric chloride. See Roucher, *Ann. chim. phys.*, [3] **27**, 353 (1849); *Compt. rend.*, **19**, 773 (1844); Thummel, *Arch. Pharm.*, **223**, 919 (1885); **227**, 589 (1889); Schroek, THIS JOURNAL, **29**, 332 (1903); and Droit, *Compt. rend.*, **152**, 960 (1911).

The constants for the equilibria represented by equations (1), (2), and (3) have been evaluated.[2]

Procedure.—The general procedure is identical to that described in earlier work.[2] The hydrochloric acid used was Grasselli c. p. acid. The samples from which the data were obtained for Table II were made by adding the same amount of Baker and Adamson Reagent mercuric oxide (6.000 g.) to each flask to which was then added 200 ml. of the standard hydrochloric acid solution. This procedure was followed in order that we might attempt to observe the progressive change in the solid phase as well as the change in solubility. The samples from which the data were ob-

TABLE I

SOLUBILITY OF YELLOW MERCURIC OXIDE IN HYDROCHLORIC ACID

Varying amounts of HgO and HCl. Samples of mercuric oxide were washed repeatedly in conductivity water previous to preparation in order to remove fine particles.

Moles HCl/1000 g. H_2O	$10^{-4} \times$ moles HgO (yellow)/1000 g. H_2O	Moles HCl/1000 g. H_2O	$10^{-4} \times$ moles HgO (yellow)/1000 g. H_2O
5.0×10^{-5}	2.47[a]	8.0×10^{-3}	18.7
1.0×10^{-4}	2.52	8.0×10^{-3}	36
3.0×10^{-4}	3.7	8.2×10^{-3}	18.1
3.0×10^{-4}	4.1	8.4×10^{-3}	18.6[a]
5.0×10^{-4}	4.9	8.6×10^{-3}	41.3
7.0×10^{-4}	6.5	9.0×10^{-3}	19.0
9.0×10^{-4}	8.4	1.0×10^{-2}	18.5
9.0×10^{-4}	7.1	1.0×10^{-2}	56
1.0×10^{-3}	6.7	1.0×10^{-2}	50.3
1.1×10^{-3}	7.2	1.2×10^{-2}	31
1.3×10^{-3}	9.8	3.0×10^{-2}	18.9
1.7×10^{-3}	11.7	5.0×10^{-2}	16.3
1.9×10^{-3}	13.0	8.0×10^{-2}	17.7
2.0×10^{-3}	13.1	1.0×10^{-1}	19.8[a]
4.0×10^{-3}	25.4	1.2×10^{-1}	22.8[a]
5.0×10^{-3}	26.2	1.2×10^{-1}	34[b]
5.0×10^{-3}	25.8[a]	1.4×10^{-1}	47[b]
6.0×10^{-3}	29.6	1.8×10^{-1}	232[a]
7.0×10^{-3}	36.6	2.0×10^{-1}	414[b]
7.0×10^{-3}	28.7	2.8×10^{-1}	534[b]
7.5×10^{-3}	20.1[a]	4.0×10^{-1}	1490[b]
		5.0×10^{-1}	1480[b]

[b] and [a] indicate approach to equilibrium from the side of saturation and unsaturation, respectively; these symbols are also used in Tables II and III.

tained for Table I were made from Baker and Adamson Reagent mercuric oxide (yellow) which was washed ten times with conductivity water before use.

The Basic Mercuric Chloride, $2HgO \cdot HgCl_2$ (Trimercuric Oxychloride).—The black solid phase in the samples (Table II) containing 0.1 *N* to 0.28 *N* hydrochloric acid was identified by mercury and chloride analysis as conforming to the formula $2HgO \cdot HgCl_2$. Basic mercuric chloride was prepared by adding mercuric oxide to 0.15 *N* solutions of hydrochloric acid, in a slight excess of the amount sufficient to convert the mercuric oxide to the basic salt in accordance with the equation

$$3HgO(s) + 2HCl \rightleftarrows 2HgO \cdot HgCl_2(s) + H_2O \quad (8)$$

The mixture was stirred vigorously, during which time its color turned from a yellow to black; this color change usually occurred within the first two hours. The solution was then decanted and the black solid washed repeatedly with conductivity water containing a small amount of hydrochloric acid. The samples used to obtain the water solubility (Table III) were washed carefully with water before they were made. The mercury analysis of four of these samples analyzed was 85.5%, the chloride analysis was 9.9% (theoretical, Hg 85.4% and Cl 10.06%).

The data are given in Tables I, II and III and are shown graphically in Figs. 1 and 2. All values are expressed in moles per 1000 g. of water.

TABLE II

SOLUBILITY OF YELLOW MERCURIC OXIDE IN HYDROCHLORIC ACID

200 ml. of standard HCl solution added to each sample containing 6.000 g. of dried reagent HgO.

Moles of HCl/1000 g. H_2O	10^{-4} × moles of HgO/1000 g. of H_2O	*p*H (glass electrode)	Character of solid phase Color	%Hg
0.00100	9.0	5.0	Yellow	
.00300	20.8[a]	4.9	Yellow	
.00500	3.18	4.9	Yellow	
.00700	40.7	4.7	Yellow and black	
.0090	28.9	4.9	Yellow and black	
.0120	30.9	5.1	Yellow and black	
.0160	29.1	5.0	Yellow and black	
.0200	22.1	4.8	Yellow and black	
.0300	15.0	5.0	Yellow and black	
.0400	10.0	5.2	Yellow and black	
.0500	21.6	5.1	Brown	
.1007	82[a]	4.0	Black	
.1210	237	4.1	Black	
.1412	387	4.2	Black	85.4
.1614	545	4.0	Black	
.2018	880	3.8	Black	85.5
.2425	1150	3.9	Black	85.6
.2832	1410		Black	85.4

Theoretical normality of 200 ml. of HCl to change 6.000 g. HgO to $2HgO \cdot HgCl_2$ is 0.0922 *N*. Theoretical % of Hg in $2HgO \cdot HgCl_2$ is 85.4%.

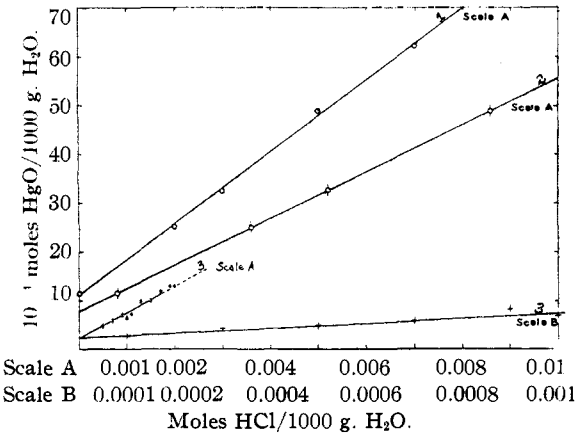

Fig. 1.—Curves 1 and 3, HCl as samples were made up; Curve 2, HCl corrected for HCl added by reaction due to the equation $2HgO \cdot HgCl_2(s) + H_2O = 3HgO + 2HCl$.

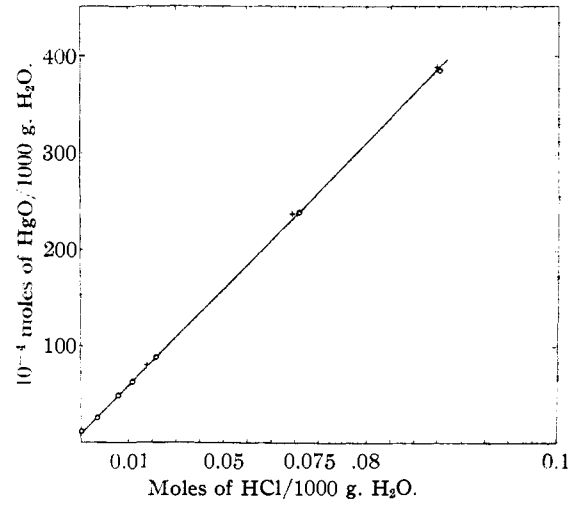

Fig. 2.—+, Table II data corrected for HCl necessary to convert HgO to $2HgO \cdot HgCl_2$; O, Table III data; data corrected for the amount of HCl added due to the reaction $2HgO \cdot HgCl_2(s) + H_2O = 3HgO + 2HCl$.

The data in Table II show a definite change in the solubility which is accompanied by a change in the solid phase from yellow HgO to black $2HgO \cdot HgCl_2$. This indicates that reactions represented by equations (4), (5), (6) and (7) are applicable to the data only below the region of the change; above this region and up to m_{HCl} = 0.1 a new solid phase is being formed, equation 8; above m_{HCl} = 0.1 a new equilibrium is estab-

lished which may be represented by equations (9), (10), (11), and (12).

The value of the water solubility of this basic chloride ($2HgO \cdot HgCl_2$) is 11.4×10^{-4} (Table III).

TABLE III

SOLUBILITY OF BASIC MERCURIC CHLORIDE $2HgO \cdot HgCl_2$ IN WATER AND IN DILUTE SOLUTIONS OF HYDROCHLORIC ACID

(Calculated as moles of HgO to compare with data in Table II.)

Moles of HCl/1000 g. H_2O	$10^{-4} \times$ moles of HgO/1000 g. H_2O	Molality of HCl at equilibrium (molality of HCl at start + $\frac{2}{3}m$ HgO. (See Eq. 8)	pH (glass electrode)	Solid phase analysis Hg, %	Cl, %
0.00	11.9				
.00	12.5				
.00	12.3				
.00	12.3				
.00	10.5				
.00	11.4				
.00	11.6				
.00	11.3				
.00	11.6				
.00	12.1				
.00	9.9				
.00	11.4				
.00	9.8				
.00	13.0				
.00	10.0				
.00	10.5				
.00	11.2				
.00	11.9				
.00	11.4				
Average	11.4	0.00076			
0.00200	25.8	0.00372	4.8	85.2	9.9
.00200	24.7	.00364	4.9		
.00300	32.5	.00517	4.8		
.00500	48.2	.00821	5.1	85.2	
.00500	49.6[a]	.00831	4.7		
.00701	62.2	.0112	5.0		
.00801	68.4	.0126	4.6		
.01002	87.8	.0159	4.6	84.8	9.8
.03003	238	.0459	4.6		
.0501	385	.0757	4.2		
.0801	626	.122	4.2		
.1008	760	.151		85.0	

Solid phase removed from flasks of samples, reported in Table II, containing HCl varying from 0.12 to 0.28 N; this material was washed with conductivity water previous to making these samples: theoretical % Hg in $2HgO \cdot HgCl_2$, 85.4%; theoretical % Cl in $2HgO \cdot HgCl_2$, 10.1%.

Above $m_{HCl} = 0.1$ Table II only one phase (black) is observed. This phase gave the mercury and chlorine analysis in agreement with the formula $2HgO \cdot HgCl_2$. Further evidence of the identity of this phase is the fact that 200 ml. of $m_{HCl} = 0.0922$ should convert the 6.00 g. of mercuric oxide to $2HgO \cdot HgCl_2$. It is to be observed from the data in Table II that the solid phase becomes homogeneous at approximately 0.1 M hydrochloric acid and the inflection of the solubility curve appears here. Additional evidence is obtained from the data in Table III also shown in Fig. 1. In this experiment samples of $2HgO \cdot HgCl_2$ were prepared by the method described above, and their water and acid solubility determined. These data were then plotted on the same graph (Fig. 1) as is used for the data in Table II. In order to compare these two sets of data the ordinate is moved to the right to $m_{HCl} = 0.0922 + m_{HCl}$ (due to solution of $2HgO \cdot HgCl_2$) which is the point at which all the HgO should be converted to $2HgO \cdot HgCl_2$ and at which the data from Tables II and III should be comparable. The agreement is excellent.

The equilibrium constants, K_4, K_{10}, K_{11} and K_{12}, are difficult to evaluate due primarily to the uncertainty of the value of a_{Cl^-}. Some information can be obtained about the relative distribution of the dissolved mercury among the forms $Hg(OH)Cl$, $HgCl_2$, $HgCl^+$ and $HgCl_3^-$ above the transition point if one makes the safe assumption that the two mercury bearing ions $HgCl^+$ and $HgCl_3^-$ only appear in appreciable concentrations at higher concentrations of mercury. The relative distribution of the dissolved mercury between $Hg(OH)Cl$ and $HgCl_2$ above the transition point is given in Table IV.

TABLE IV

APPROXIMATE DISTRIBUTION OF DISSOLVED MERCURY IN THE REACTION OF $2HgO \cdot HgCl_2$ WITH HCl

Calculated from the equation below; smooth data from graph.

C Moles of added HCl/1000 g. H_2O	S $2HgO \cdot HgCl_2$ expressed as 10^{-4} moles HgO/1000 g. H_2O	X % HCl transformed to $HgO \cdot HCl$ assuming only $HgO \cdot HCl$ and $HgCl_2$ are formed
0.001	18.4	49
.0015	22.0	32
.002	25.6	24
.004	40.3	12
.006	55.3	8
.008	70.0	6
.01	85.3	4
.02	161	3
.04	308	1

$$X = \frac{(S/C) - 0.75}{2.25}$$

The Transition.—No definite statement can be made of the exact value of m_{HCl} at the

transition point. The problem yet to be solved is to determine the equilibrium concentrations of HCl, HgO and 2HgO·HgCl at the triple point.

Summary

The solubilities of mercuric oxide and of basic mercuric chloride, $2HgO \cdot HgCl_2$, have been measured in hydrochloric acid solutions. A break occurs in the solubility relationships due to the formation of a new solid phase ($2HgO \cdot HgCl_2$). This basic mercuric chloride, $2HgO \cdot HgCl_2$, has been prepared and identified; the water solubility is 11.4×10^{-4}. The relative distribution of mercury among several different ion species is indicated.

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[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

Adsorption and the Energy Changes[1] at Crystalline Solid Surfaces

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Theory

Adsorption is accompanied by a change both in the total and in the free surface energy of a surface. The classical relation of J. W. Gibbs[2] for interfaces between fluids has been used extensively and certainly must be regarded as valid when properly applied. The question of the applicability of the theorem to the interface between solids and fluids must be considered, and we are fortunate that Gibbs has discussed the problem in detail in the case in which the solid is anisotropic.

Thus, if the total surface energy, E_{so}; surface entropy, S_{so}; surface densities of chemical species, Γ_i; chemical potentials, μ_i; and temperature, T, are used, it is possible to define a quantity, ζ, for the arbitrarily restricted case of a system of two components by the equation[3]

$$\zeta = E_{so} - TS_{so} - \mu_1\Gamma_1 - \mu_2\Gamma_2 \qquad (1)$$

In Gibbs' words, "The quantity ζ evidently represents the tendency to contraction in that portion of the surface of the fluid which is in contact with the solid. It may be called *the superficial tension of a fluid in contact with a solid*. Its value may be either positive or negative.

"It will be observed for the same solid surface and for the same temperature but for different liquids the values of γ_{sf} (in all cases to which the definition of this quantity is applicable) will differ from those of ζ by a constant, *viz.*, the value of γ_{so} for the solid surface in a vacuum."

Obviously, ζ is defined by

$$\zeta = \gamma_{sf} - \gamma_{so} = -\pi \qquad (2)$$

or, the spreading pressure, π, is equal to the difference between the free surface energy of the clean solid surface (in a vacuum) and the free surface energy when in equilibrium with a chemically dissimilar fluid component (*i. e.*, gas or liquid).

Utilizing Gibbs' general thermodynamic methods, from equation (1), it is possible to obtain for a system consisting of a crystalline adsorbent and one adsorbate

$$d\pi = S_{so}dT + \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 \qquad (3)$$

If isothermal conditions are maintained, and if the Gibbs plane from which adsorption is reckoned is chosen so that the surface density of adsorbent, Γ_1, is zero, one may write

$$d\pi = \Gamma_2^{(1)} d\mu_2$$

or

$$\Gamma_2^{(1)} = \left(\frac{\partial \pi}{\partial \mu_2}\right)_{T,\, P,\, \mu_1} \qquad (4)$$

For the case in which the fluid contiguous to the solid surface is a gas or a vapor

$$d\mu_2 = RT\, d \ln f_2 \qquad (5)$$

where f_2 is the fugacity, and for vapors at low pressures

$$RT\, d \ln f_2 = RT\, d \ln p_2 \qquad (6)$$

is true with sufficient accuracy, so that equation (4) may be written as

$$d\pi = RT\Gamma_2^{(1)} d \ln p_2 \qquad (7)$$

where p_2 is to be taken as the equilibrium pressure of a gas or vapor above the crystal surface upon which adsorption has occurred.[4]

(1) Original manuscript received February 4, 1942.

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(2) J. W. Gibbs, "Collected Works," Longmans, Green & Co., New York, N. Y., 1928, p. 314.

(3) It will be noticed that we have taken the liberty of modifying part of Gibbs' original nomenclature in order to bring it into approxi-

(4) Extensive calculations to establish the correctness of Equ.