

The Solubility of Elemental Mercury Vapor in Water

Isao SANEMASA

Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami-machi, Kumamoto 860

(Received September 17, 1974)

The solubility of mercury vapor in water has been measured by means of atomic absorption spectrophotometry over the temperature range of 5–60 °C under atmospheric pressure. The aqueous solubility obeys Henry's law at each temperature. The solubilities and the Henry coefficients are reported. From the solubility data, the heat of the solution of mercury vapor in water is found to be -5.3 kcal/mol. The relationship between the Henry coefficient, k , and the solution temperature, T , is expressed by $\log k = -1078 \times 1/T + 6.250$. From this equation, the solubilities at 70–100 °C are estimated. The solubility of the mercury vapor in sea water has also been measured over the temperature range of 5–30 °C. A salting-out effect on the solubility is observed. The practical application of the aqueous solubility of the mercury vapor is discussed from the analytical point of view.

Bonhoeffer and Reichart¹⁾ showed that the absorption spectrum of an aqueous solution of mercury was essentially the same as that of mercury vapor. At about the same time, Stock *et al.*²⁾ reported the solubilities of the metallic mercury in water. Since then, the solubilities of mercury have been studied by many workers. There is, however, a considerable disagreement among the literature values. This may be ascribed to the different experimental techniques used. The conventional techniques for the measurement of the mercury solubilities are as follows: colorimetric analysis, Pariaud and Archinard;³⁾ radioactive-tracer technique, Moser and Voigt;⁴⁾ neutron-activation method, Choi and Tuck;⁵⁾ atomic absorption spectrophotometry, Glew and Hames.⁶⁾ The most recent work is that by Onat,⁷⁾ who studied the dissolved mercury by means of ultraviolet spectrophotometry. The principle of measuring the dissolved mercury employed by Moser and Voigt and by Onat is different from that of other workers; it is based on the disproportionation reaction of the mercurous dimer into mercuric ions and free mercury. However, the procedures to attain the solubility equilibrium are essentially similar to those employed by other workers: they brought water into contact with metallic mercury. In the present work, mercury is treated as a vapor, and the solubility is determined based on Henry's law. The present study is different in this respect from those of the other workers.

Mercury, because of its high vapor pressure at room temperature, is introduced into the atmosphere through the impingement of the vapor and the fallout of particulate matters derived from the industrial process. During the past few years, considerable attention has been directed toward the potential hazards of mercury and its compounds in our environment. There have also been several articles^{8–11)} dealing specifically with the presence of mercury in air.

The generally accepted procedure for the determination of trace amounts of mercury is the cold-vapor atomic absorption technique, because it exhibits a high sensitivity. It is essentially based on a reduction-aeration method found by Kimura and Miller;¹²⁾ mercury present in solution as Hg(II) is reduced with Sn(II), and the resulting mercury vapor is separated by aeration. The most commonly utilized method at present was originally described by Hatch and Ott,¹³⁾ who combined the closed system reduction-aeration

principle with atomic absorption spectrophotometry. The aqueous solubility of mercury vapor is, therefore, a common topic in analytical laboratories.

There are various forms of mercury found in nature, such as metal, inorganic, and organic compounds. Although most of the mercury reported in fish tissue is in the methyl form,¹⁴⁾ very little methylmercury has been discovered in sediments or river waters. Spangler *et al.*¹⁵⁾ demonstrated that demethylation processes by microbes in sediments probably reduce some or all of the methyl form to metallic mercury. It is also of interest, from this aspect, to study the aqueous solubility of elemental mercury.

Experimental

Reagents. All the chemicals were of an analytical reagent grade unless otherwise specified. The solutions used were: stannous chloride, 10% solution in 1 M HCl; sulphuric acid, 50% solution; potassium permanganate, 6% solution. The standard mercury stock solution of 0.5 mg/ml was prepared by dissolving the required amount of mercury (II) chloride in water. This solution was used to prepare a working standard containing 0.5 mg/l by dilution before each use. The metallic mercury was purified by distillation under reduced pressure after the air oxidation of the contaminated metal through successive aeration in water and by passing it through a column filled with a diluted HNO₃ solution.

Apparatus. The atomic absorption measurements were made with a Hitachi Model 508 atomic absorption spectrophotometer equipped with a mercury hollow-cathode lamp. A 10-cm-long gas cell with a 9.1-cm² cross-section and quartz windows was used. The instrumental settings were as follows: hollow-cathode lamp current, 6 mA; wavelength, 253.7 nm; band width, 0.32 nm. The solubility apparatus used was a simple closed system, as is shown in Fig. 1. It was composed of four glass flasks, a circulating pump (P) the metallic part of which was covered with plastic, and polyethylene tubes to connect them. Flask A is a 300 ml three-necked flask; the center neck is stoppered, while the other two are connected to a condenser and a gas inlet-type adapter with a stopcock. Flask B is a 1-l three-necked flask; the center neck is stoppered, while the other two are connected to a gas inlet-type adapter and an adapter, each with a stopcock. Flasks C and D, used as traps for the water vapor, are gas-washing-type, long-necked bottles with capacities of 500 ml and 2 l respectively. Flask A and Flasks B, C, and D were immersed in separate thermostats controlled within ± 0.05 °C. The inlet of the circulating pump was connected

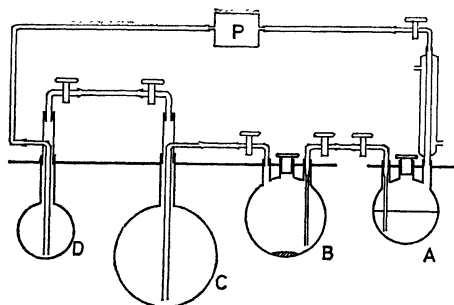


Fig. 1. Mercury vapor solubility apparatus.

to Flask A through the condenser, which was maintained at the same temperature as Flask B by circulating the water of the thermostat. The outlet of the pump was connected to Flask B, before which Flasks C and D were placed. The temperature of the room was always maintained higher than that of Flask B. The pressure in the closed system was always kept under atmospheric pressure.

Procedure. About a 20-g portion of metallic mercury is dropped into Flask B. A water sample (100 to 200 ml) is then poured into Flask A. After the mercury and the solution reach the desired temperatures, mercury vapor is introduced, bubbled into Flask A, and circulated by means of the pump. The circulation rate is adjusted to 100 to 200 ml/min. by using a Variac. After solubility equilibrium is attained, a suitable aliquot (1 to 20 ml) of the solution is withdrawn from Flask A and immediately added to a reduction-aeration bottle in the atomic absorption spectrophotometer. Measurements were made at least three times.

Measurement. The analytical procedure for determining the dissolved mercury by the flameless atomic absorption method is essentially similar to that reported by Omang.¹⁶⁾ Introduce a 100 ml portion of distilled water, 2 ml of 9 M sulphuric acid, and 2 ml of 10% tin(II) chloride solution into a 300-ml reduction-aeration bottle. Connect the bottle to an aeration apparatus equipped with a circulating pump and exhaust any mercury arising from contaminated reagents. When the recorder pen has returned to the base line, add the sample solution to the bottle and turn on the circulating pump at a constant flow rate of 1.5 l/min. Record the absorption peak of the mercury vapor. Carry the mercury working standard (0.05 to 0.5 μg) in the same manner as in the sample. In this case, care must be taken to adjust the total volume and the salt concentration in the bottle to make them constant. Determine the mercury concentration in the sample solution by means of a calibration curve.

Results and Discussion

The Time Required for the Attainment of the Solubility Equilibrium.

The attainment of an equilibrium is important for solubility determinations and is checked in the following manner. A part of the solubility apparatus is disconnected and combined directly to the gas cell of the atomic absorption spectrophotometer. Drop metallic mercury into Flask B in the same manner as has been described in the Experimental section in the absence of water in Flask A, and then turn on the circulating pump and the recorder. The absorbance reading then begins to rise, reaches a maximum within 5 to 30 min. in accordance with the surface area of the mercury, and thereafter remains constant. Add an aqueous solution of about 100 ml

to Flask A and monitor the absorbance reading. This monitoring shows that the reading, after a temporary sinking, returns slowly to the former constant line within 10 to 30 min. From the practical point of view, the liquid phase will reach equilibrium with the circulating mercury vapor within an hour.

The Effect of Oxygen on the Solubility. It has been said that mercury is readily oxidized in humid air.²⁾ In order to clarify this, experiments were made under conditions of both sufficiently aerating and bubbling nitrogen gas through the water. As a result, no appreciable differences in the solubility of mercury vapor were observed under the present experimental conditions.

The State of Mercury Gas Dissolved in Aqueous Solutions.

In order to obtain information about the state of the mercury gas dissolved in pure and sea water, atomic absorption measurements were made with and without the addition of a reductant, Sn(II)-H₂SO₄ solution, to sample solutions in a reduction-aeration bottle. In the absence of the reductant, the readings of the absorption peaks were lowered by 1 to 2%. This is probably because of the relatively high salt concentrations in the liquid phase upon the addition of the reductant—that is, the salting-out effect. Indeed, the absorption peak increased gradually with an increase in the additional reductant. The same situation was also found in the case of the standard mercury solution. From the facts mentioned above and from the fact that the solubility obeys Henry's law, it may be concluded that the mercury gases dissolved in pure and sea waters are in the elemental form.

Solubility of the Mercury Vapor in Water. In Figs. 2 and 3, the solubilities of mercury vapor in water in the temperature range from 5 to 60 °C are plotted against its vapor pressure; they are in equilibrium with the metallic mercury at the desired temperatures. The solubility at 5 °C may be less reliable. Figures 2 and 3 show that the aqueous solubility of mercury vapor obeys Henry's law at each solution temperature except at 5 °C. When the temperatures

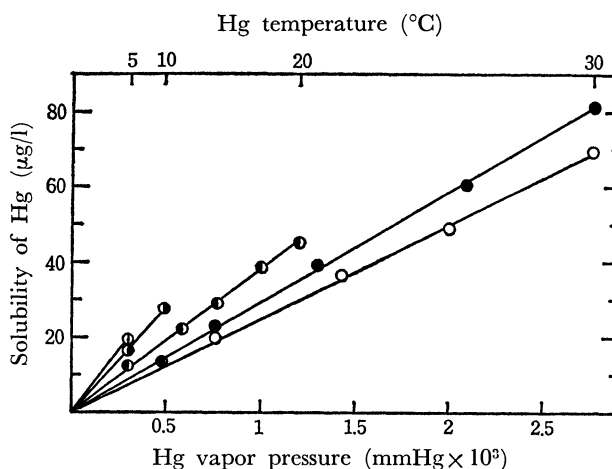


Fig. 2. The dependence of mercury solubility on mercury vapor pressure in pure water at 5 °C (○), 10 °C (◐), 20 °C (●), 30 °C (●) and in sea water at 30 °C (○).

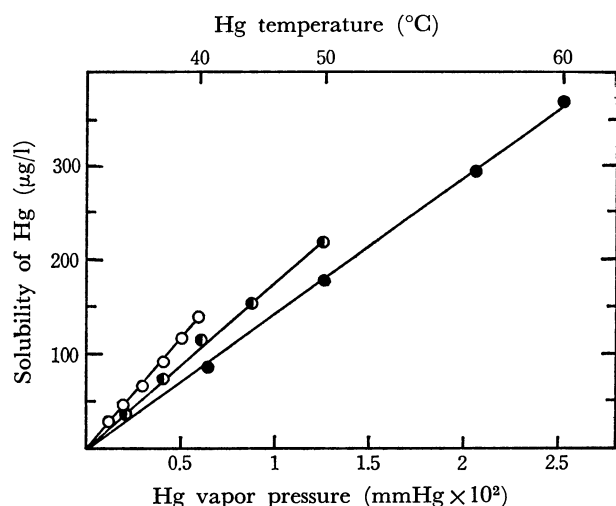


Fig. 3. The dependence of mercury solubility on mercury vapor pressure in pure water at 40 °C(○), 50 °C(●), and 60 °C(●).

TABLE 1. Hg SOLUBILITY AND HENRY COEFFICIENTS

Temp. (°C)	Solubility (µg/l) ^a	Henry coefficient
Pure water		
5	19.2	233
10	27.4	262
20	45.0	391
30	81.3	500
40	137	650
50	218	852
60	368	1010
70	5.6×10^3	13×10^3
80	8.5	15
90	12	19
100	18	23
Sea water		
5	17.2	
10	23.6	
15	31.6	
20	40.6	
25	54.9	
30	69.7	

a) Solubility is expressed in µg/l for convenience which is transformed into mole fraction by multiplying 8.98×10^{-11} .

of mercury are higher than those of solutions, the solubility values become lower than those expected from Henry's law because of the condensation of the vapor. The solubility data are summarized in Table 1, together with the Henry coefficients. The Henry coefficients are determined by dividing the partial pressures of mercury vapor (atm) by the mole fractions of the mercury dissolved.

The Temperature Dependence of the Solubility. The Henry coefficients are plotted in Fig. 4 according to the van't Hoff equation:

$$d \ln k / dT = \Delta H / RT^2 \quad (1)$$

where k is the Henry coefficient. The heat of solu-

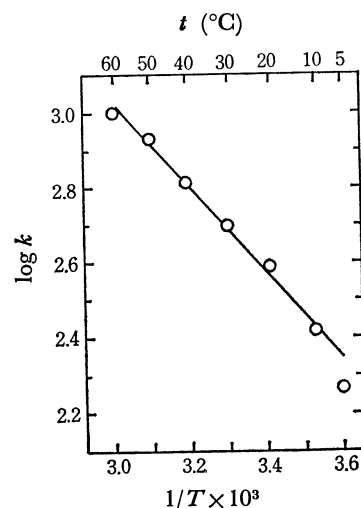


Fig. 4. $\log k$ vs. $1/T$ plot. The temperature dependence of solubility of mercury vapor in water.

tion, ΔH , is calculated from the slopes of the $\log k$ vs. $1/T$ plots to be -5.3 kcal/mol. The relationship between the Henry coefficient and the solution temperature is expressed in the following empirical equation:

$$\log k = -1078 \times 1/T + 6.250 \quad (2)$$

The solubility data and the Henry coefficients at 70–100 °C listed in Table 1 are calculated from Eq. (2) and the mercury-vapor pressures at the corresponding solution temperatures on the assumption that Henry's law holds up to those pressures.

Comparison of the Present Results with the Literature. This paper has presented the solubility results of mercury vapor in water. The aqueous solubility of mer-

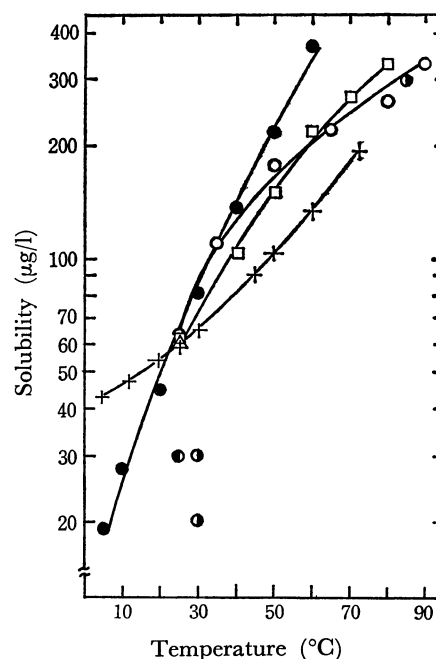


Fig. 5. Comparison of the solubilities reported in the literature: ●, this work; □, Onat; ○, Choi and Tuck; +, Glew and Hames; △, Moser and Voigt; ○, Pariaud and Archinard; ●, Stock *et al.*

TABLE 2. SOLUBILITY OF MERCURY AT 25 °C

Solubility ($\mu\text{g/l}$)	Literature
63.9	This work ^{a)}
63.1	Choi and Tuck
58.8	Glew and Hames
61	Onat
60	Moser and Voigt
30	Pariaud and Archinard
20–30	Stock <i>et al.</i> ^{b)}

a) Calculated from Eq. (2). b) Value at 30 °C.

cury in the metallic and gaseous states should be identical, provided that the dissolved metal mercury is in the elemental form. The results reported in the literature are illustrated in Fig. 5, together with those of the present work. The solubility data at 25 °C, summarized in Table 2, are in good agreement except for the earlier measurements by Stock *et al.* and Pariaud and Archinard. Above 50 °C, however, the present results are higher than those reported by other workers. Below 20 °C, the present results are considerably lower than those by Glew and Hames. However, their results are definitely too high, in view of the temperature dependences of the other two studies. The discrepancies in the present results at moderately higher temperatures may be caused by the different procedures used to attain the solubility equilibrium.

The Solubility in Sea Water. The solubility of mercury vapor in sea water was measured in the interest of practicality. The total mercury contained in the sample was analyzed prior to the solubility measurements. The blank concentration was found to be less than 0.1 $\mu\text{g/l}$. For this low content, the solubility data obtained were uncorrected. As is shown in Fig. 2, it is also confirmed that the solubility of mercury vapor in sea water at 30 °C obeys Henry's law. The solubility data at 5–30 °C are given in Table 1. It can be said, from Fig. 2 and Table 1, that the salting-out effect is observed on the aqueous solubility of mercury vapor, just as is observed in atomic absorption measurements. "Salting-out" is the decrease in the solubility of a non-electrolyte in ionic solutions.¹⁷⁾

The Practical Application of the Aqueous Solubility of Mercury Vapor. According to the literature, the concentrations of mercury vapor in several laboratory atmospheres were determined to be 2–8,⁸⁾ 0.012,⁹⁾

or 1–30 $\mu\text{g/m}^3$.¹¹⁾ Based on the emission standard for mercury (1 $\mu\text{g/m}^3$) promulgated by the U. S. Environmental Protection Agency,¹⁰⁾ the estimation of the aqueous solubility of the mercury vapor has been attempted. As a result, it has been found to be 0.0034 $\mu\text{g/l}$ at 20 °C. In general, the concentration range of mercury in natural waters is from 0.5 to 364 ng/l.¹⁸⁾ Because of its low abundance, care must be taken in the discussion of the results when analytical experiments are made in the laboratory of the several $\mu\text{g/m}^3$ level.

The author is indebted to Professor Hideo Nagai and Mr. Toshio Deguchi of Kumamoto University for their encouragement and discussions. Thanks are also due to the members of the Marine Biological Station of Kumamoto University for sampling the sea water.

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