

VOLATILITY OF MERCURY IN WATER

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Summary

The rate of volatilization of mercury and oxygen from the aqueous phase to the gas phase was studied by bubbling with nitrogen. The ratio, $K_L^{\text{Hg}}/K_L^{\text{O}_2}$, of the mass transfer coefficient of mercury to that of oxygen was determined in the temperature range 278–308 K. The ratio of 0.94 ± 0.08 which was obtained was found to be higher than that for 19 other substances, such as krypton, radon, ethylene, methylene chloride and benzene, quoted in the literature. Thus, mercury was found to be readily volatilized from the aqueous to the gas phase, despite having a much lower vapor pressure and a higher molecular weight than the other substances.

Introduction

It is well known that mercury is transported widely into the environment. Transport from the aqueous phase to the gas phase can be an important environmental pathway for mercury. The rate equation for this transport has been analyzed using the two-film model [1–5]. The value of the mass transfer coefficient for transport varies with the conditions, such as mixing and temperature. However, Smith et al. [2] showed that the ratio of the mass transfer coefficient of a compound to that of oxygen is constant over a wide range of conditions when the transport of the compound is controlled by the mass transfer rate in the aqueous phase.

In this work, the volatilization rate of mercury is investigated and the ratio of the mass transfer coefficients of mercury and oxygen determined, because no information on this is available in the literature, despite the serious need for this in environmental science.

Experimental

All the chemicals used in this experiment were of analytical reagent grade. The schematic diagram of the experimental apparatus is shown in Fig. 1, where a gas-washing type volatilization vessel of volume $0.5 \times 10^{-3} \text{ m}^3$, equipped with a 0.025 m diameter spherical sintered-glass filter, is connected

to an atomic absorption spectrophotometer for mercury analysis, and to a dissolved oxygen analyzer for oxygen analysis.

The volatilization rate of mercury was measured as follows: an aqueous mercuric chloride solution at a level of 10^{-10} mol/m³ (below the value of elemental mercury solubility in water [9]) was prepared in the vessel. By the addition of hydrazine hydrate [9,10] to the aqueous solution as a reducing agent, the mercuric chloride was reacted quickly and completely to elemental mercury. The elemental mercury thus formed was immediately volatilized in nitrogen at a constant flow rate and temperature, and was conducted to the absorption cell in the spectrophotometer. It was then absorbed by $\text{KMnO}_4 + \text{H}_2\text{SO}_4$. The concentration of volatilized mercury was continuously measured by the atomic absorption analyzer at 253.7 nm. The rate coefficient of mercury was determined by fitting the absorbance data to eqn. (9), described later.

In order to measure the oxygen volatilization rate, distilled water saturated with dissolved oxygen was prepared in the vessel, as shown in Fig. 1. By bubbling with nitrogen at a constant gas flow rate and temperature, the oxygen dissolved in the water was purged into the nitrogen. The rate coefficient of oxygen was determined from the variation with time of oxygen concentration in the water, which was directly measured by a polarographic-type dissolved oxygen analyzer (model UC-11, Central Science Co.).

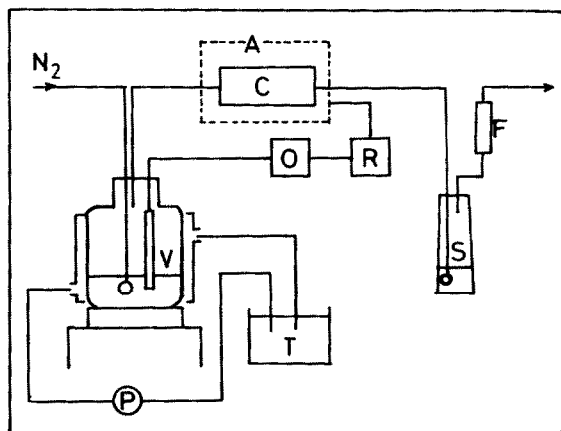


Fig. 1. Schematic diagram of apparatus. A: atomic absorption spectrophotometer, C: absorption cell, F: flow meter, O: dissolved oxygen analyzer, P: pump, R: recorder, S: ($\text{KMnO}_4 + \text{H}_2\text{SO}_4$) absorber, T: thermostat, V: volatilization vessel.

Results and discussion

In a semi-batch system for bubbling, as shown in Fig. 1, a volatile contaminant in water is continuously volatilized from the aqueous phase to the gas phase. Using the two-film model for mass transfer, the mass transfer rate, N (mol/s), may be expressed in terms of an overall mass transfer coefficient, K_L

(m/s) (or a volumetric mass transfer coefficient, $K_L a$ (s^{-1})), and an overall concentration difference:

$$N = -V_L dC_L/dt = K_L a (C_L - p/H) V_L \quad (1)$$

where C_L (mol/m^3) is the concentration of a contaminant in the aqueous phase, t (s) is the volatilization time, a (m^{-1}) is the interfacial area per unit volume of the aqueous phase, p (Pa) is the Henry's constant, and V_L (m^3) is the volume of the aqueous phase.

Consideration of the mass balance of the contaminant in the gas phase for bubbling at a constant gas flow rate and temperature gives the following equation:

$$N = C_G Q = p q V_L / RT \quad (2)$$

where C_G (mol/m^3) is the concentration of the contaminant in the gas phase, Q (m^3/s) is the gas flow rate, q (s^{-1}) is the gas flow rate per unit aqueous solution ($= Q/V_L$), R ($\text{m}^3 \text{ Pa/mol K}$) is the gas constant, and T (K) is the absolute temperature. From eqns. (1) and (2), eqn. (3) is obtained:

$$p = [1/H + (1/K_L a)(q/RT)]^{-1} C_L \quad (3)$$

Integration of eqn. (1) along with eqn. (3) (which satisfies the initial condition $C_L = C_{L0}$ at $t = 0$) yields:

$$C_L/C_{L0} = \exp(-K_v t) \quad (4)$$

where K_v (s^{-1}) is the rate coefficient for bubbling as expressed by eqn. (5):

$$1/K_v = 1/K_L a + RT/Hq \quad (5)$$

The rate coefficient, K_v , can be determined from the slope of a linear plot of $\log(C_L/C_{L0})$ against the volatilization time, t , and hence the volumetric mass transfer coefficient, $K_L a$, can be calculated from eqn. (5).

The rate coefficient of oxygen was readily determined by using eqn. (5) (as shown in Table 1). On the other hand, in the measurement of mercury volatilization rate, the mercury concentration in the aqueous solution, C_L , could not be obtained directly, but was instead measured through the absorbance, which gave the concentration of mercury vapor. Therefore, eqn. (4) cannot be directly applied to determine the rate coefficient of mercury. In order to use eqn. (4), it is necessary to clarify the relationship between C_L and the absorbance, which was carried out as described below.

It is convenient to express the absorbance, A (m), as the height of the absorbance peak on the recorder of the absorption spectrophotometer. If the total amount of mercury contained in an aqueous volume V_L , with its initial concentration C_{L0} , is volatilized from the aqueous phase by bubbling at a gas flow rate Q , the mass balance is expressed by eqn. (6), and the area of the ab-

sorbance curve is given by eqn. (7):

$$V_L C_{L0} = \int_0^{\infty} C_G Q dt \quad (6)$$

$$\alpha C_{L0} = \int_0^{\infty} \beta A dt \quad (7)$$

where α ($\text{m}^2/\text{mol m}^{-3}$) is the absorbance area per unit mercury concentration in the aqueous phase, and β (m/s) is the chart speed in the recorder. As the absorbance A is proportional to the mercury vapor concentration C_G , their relationship (eqn. 8) is derived from eqns. (6) and (7):

$$C_G = p/RT = \frac{A}{(\alpha/\beta)q} \quad (8)$$

Substituting eqn. (3) into eqn. (8), the relationship between A and C_L is given by eqn. (9):

$$A = (\alpha/\beta)K_v C_L = (\alpha/\beta)C_{L0}K_v \exp(-K_v t) \quad (9)$$

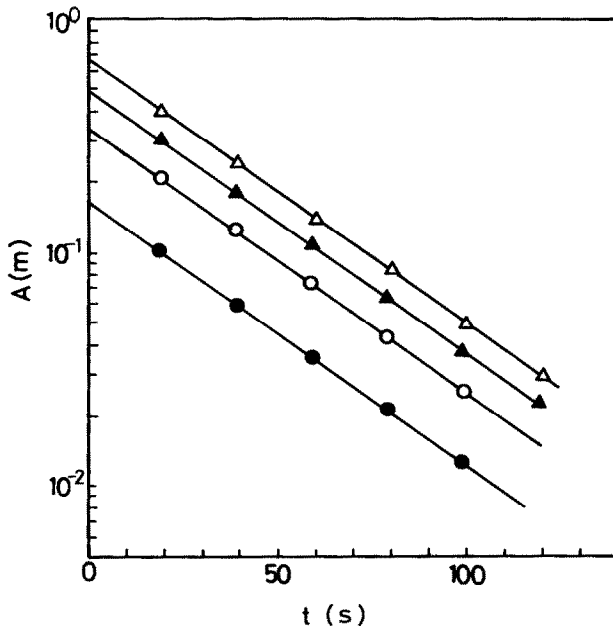


Fig. 2. Effect of initial mercury concentration on the relationship between absorbance, A , and time, t . Nitrogen flow rate: $0.5 \times 10^{-4} \text{ m}^3/\text{s}$, volume of aqueous phase: $0.2 \times 10^{-3} \text{ m}^3$, temperature: 298 K, chart speed: 10^{-3} m/s , initial mercury concentration $\times 10^{10} \text{ mol/m}^3$: ● - 0.5, ○ - 1.0, ▲ - 1.5, △ - 2.0.

From the form of eqn. (9) it can be seen that from a linear plot of $\log A$ against t , K_v can be determined from the slope without the need for measuring the mercury concentration in the aqueous solution.

Figure 2 shows the relationship between A and t , which was measured in the initial mercury concentration ranging from 0.5×10^{-10} to 2.0×10^{-10} mol/m³ at a gas flow rate of 0.5×10^{-4} m³/s at 298 K and a chart speed of 10^{-3} m/s. From the slope of the plot in Fig. 2, the rate coefficients of mercury were readily obtained. They were independent of the initial mercury concentration. Figure 3 shows the relationship between the absorbance at $t = 0$ (that is corresponding to $(\alpha/\beta)C_{L_0}K_v$) and the initial mercury concentration, C_{L_0} . Apparently, the absorbance thus obtained was directly proportional to the initial concentration. The α/β value of 1.28×10^5 m s/mol m⁻³ calculated from the slope in Fig. 3 was also in a good agreement with that of 1.27×10^5 obtained by measurements of the area of the absorbance peak under the same conditions in Fig. 2. These results were found to agree well with those predicted from eqn. (9). Therefore, the rate equation of eqn. (9) expressed in terms of the absorbance can be used for the determination of the rate coefficient of mercury from the aqueous solution.

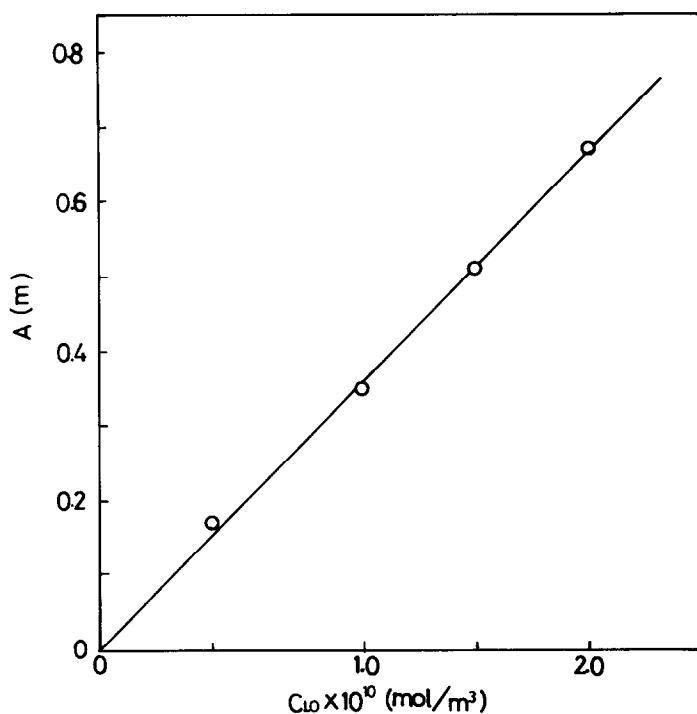


Fig. 3. Relationship between the absorbance, $A (= (\alpha/\beta)C_{L_0}K_v)$, at $t = 0$ and the initial mercury concentration, C_{L_0} . Nitrogen flow rate: 0.5×10^{-4} m³/s, temperature: 298 K, chart speed: 10^{-3} m/s.

TABLE 1

Rate coefficient for bubbling^a, K_v , and volumetric mass transfer coefficient, $K_L a$, for mercury and oxygen at 298 K

$Q \times 10^{-4}$ (m ³ /s)	$K_v^{\text{Hg}} \times 10^2$ (s ⁻¹)	$K_v^{\text{O}_2} \times 10^2$ (s ⁻¹)	$K_L^{\text{Hg}} a \times 10^2$ (s ⁻¹)	$K_L^{\text{O}_2} a \times 10^2$ (s ⁻¹)
0.17	0.65	0.91	0.81	0.91
0.25	1.31	1.74	1.78	1.75
0.33	1.85	2.83	2.56	2.85
0.42	2.26	3.42	3.10	3.45
0.50	2.59	3.52	3.50	3.54
0.58	2.93	4.03	3.91	4.05
0.67	3.48	5.16	4.71	5.19
0.75	3.88	5.67	5.23	5.70
0.83	4.30	5.92	5.79	5.95

^a The volume of aqueous phase is 0.2×10^{-3} m³.

Table 1 shows the effect of the gas flow rate on the rate coefficients, K_v , and the volumetric mass transfer coefficients, $K_L a$, of mercury and oxygen at 298 K. The values of $K_L a$ were calculated from eqn. (5) using a value of Henry's constant of 993 m³ Pa/mol [11,12] for mercury and of 79240 [13] for oxygen at 298 K. Figure 4 shows the relationship of the volumetric mass transfer coefficient between mercury and oxygen. The slope of the linear plot gives the ratio $K_L^{\text{Hg}}/K_L^{\text{O}_2}$. The effects of temperature in the range 278–308 K and of V_L in the range 0.1×10^{-3} – 0.35×10^{-3} m³ on the ratio showed

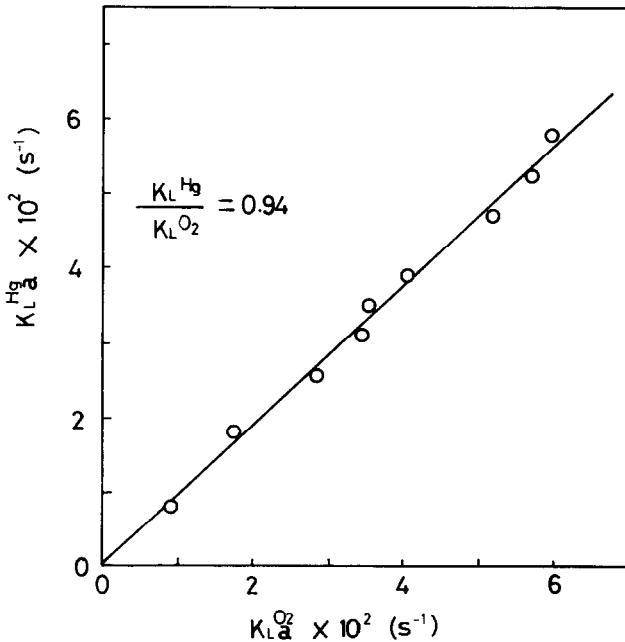


Fig. 4. Ratio, $K_L^{\text{Hg}}/K_L^{\text{O}_2}$, of mass transfer coefficient of mercury to that of oxygen at 298 K.

that both the rate coefficient of mercury and of oxygen increased with increasing temperature and decreasing V_L ; however, their ratio remained constant. The ratio of $K_L^{\text{Hg}}/K_L^{\text{O}_2}$ obtained was found to be 0.94 ± 0.08 .

When the volatilization rate is controlled by the mass transfer rate in the aqueous phase, the mass transfer coefficient can be estimated from the relationships $K_L \propto 1/d$ [6,8] or $K_L \propto D_L$ [2,14], where d and D_L are the molecular diameter and the diffusivity in the aqueous phase, respectively. Mackay et al. [5] showed that the mass transfer rate in the aqueous phase controlled the volatilization rate when the value of Henry's constant was greater than about $500 \text{ m}^3 \text{ Pa/mol}$. Therefore, it is apparent that the above relationships can be applicable to the mass transfer of both mercury and oxygen. The ratio measured in this work agreed approximately with the values 0.83 or 1.2 estimated from the ratio of the molecular diameters or the diffusivities of mercury and oxygen, respectively.

Table 2 shows the ratio of the mass transfer coefficients for elements, compounds, or contaminants reported in the literature [2-4,6-8]. These ratios show that mercury is readily volatilized from the aqueous phase to the gas phase, and that mercury volatilization occurs much faster than has been generally appreciated.

TABLE 2

Ratio, $K_L^i/K_L^{\text{O}_2}$, of the mass transfer coefficient of contaminant i to that of oxygen

Contaminant i	Molecular weight	$K_L^i/K_L^{\text{O}_2}$
Methylene chloride	84.94	0.74 [4], 0.655 [7]
Chloroform	119.39	0.57 [2], 0.536 [4], 0.655 [7]
Carbon tetrachloride	153.84	0.598 [4], 0.63 [7]
Freon-12	120.91	0.629 [4]
1,1-Dichloroethane	98.96	0.71 [2]
1,1,1-Trichloroethane	133.40	0.591 [4]
Ethylene	28.05	0.87 [7]
1,1-Dichloroethylene	96.94	0.62 [3]
Trichloroethylene	131.39	0.57 [2], 0.602 [4]
Tetrachloroethylene	165.83	0.52 [2], 0.55 [3], 0.607 [4]
Propane	44.10	0.72 [7]
Benzene	78.11	0.56 [2], 0.53 [3], 0.655 [7]
Toluene	92.14	0.53 [3], 0.655 [7]
1,2,4-Trimethylbenzene	120.19	0.39 [3]
1,4-Dichlorobenzene	147.00	0.39 [3]
PCB (Aroclor 1016)	—	0.25 [8]
(Aroclor 1242)	257.55	0.22 [8]
Krypton	83.80	0.81 [6]
Radon	222.0	0.70 [6]
Mercury	200.59	0.94 ^a

^a This work.

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