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The Mercury Volatilization Rate from Water to the Atmosphere

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The volatilization rate of mercury was studied, together with the oxygen reaeration rate, in a laboratory scale under various mixing conditions. The rates of both mercury and oxygen were controlled by mass transfer in the aqueous phase. The obtained ratio of the mercury-volatilization rate constant to the oxygen-reaeration rate constant was 0.94 at temperatures ranging from 283 to 303. If the oxygen-reaeration rate constant is available in a real-water body or in a wastewater-treatment facility, multiplying its value by the ratio of 0.94 permits the determination of the volatilization rate constant of mercury without the direct measurement of the mercury.

It is well known that contaminants such as mercury, DDT, and PCB have been transported widely throughout global environments. The volatilization of contaminants from natural water bodies to the atmosphere has been considered to be a very important step in the environmental-pollution process.

A mass balance for the volatilization of a contaminant, i, from well-mixed water into the atmosphere is given by Eq. 1:

$$-\mathrm{d}C^{(i)}/\mathrm{d}t = K_V^{(i)}(C^{(i)} - p^{(i)}/H^{(i)}), \tag{1}$$

where C is the concentration of the contaminant in the water; t is the time; K_v is the volatilization rate constant; p is the partial pressure of the contaminant in the atmosphere, and H is Henry's law constant. The subscript (i) denotes the component i. According to the two-film model, $K_V^{(i)}$ is given by Eq. 2:

$$K_V^{(i)} = K_L^{(i)}a = [1/k_L^{(i)} + (RT/H^{(i)})(1/k_G^{(i)})]^{-1}a, \tag{2}$$

where K_L is the overall mass-transfer coefficient based on the liquid-phase concentration; k_L and k_G are the mass-transfer coefficients in liquid and gas films respectively; a is the interfacial contact area per liquid volume; R is the gas constant, and T is the absolute temperature.

The actual environmental-water body generally comes in contact with the atmosphere on its free surface; therefore, a is given by the reciprocal of the depth of the water, L. Thus, the overall volatilization rate constant of a component, i, from an environmental-water body, $K_{V(env)}^{(i)}$, is expressed by:

$$K_{V(env)}^{(i)} = (1/L)[1/k_{L(env)}^{(i)} + (RT/H^{(i)})(1/k_{G(env)}^{(i)})]^{-1}. \tag{3}$$

The subscript (env) means the environmental-water body. Since the coefficients, $k_{L(env)}$ and $k_{G(env)}$, depend greatly on the hydrodynamic situation of both water and atmosphere, it is necessary, for the direct evaluation of $K_{V(env)}^{(i)}$, according to Eq. 3, to grasp the mixing situation of the system quantitatively. This is, however, a very difficult matter, except the oxygen-reaeration rate constant, $K_{V(env)}^{(O_2)}$,1–3) of $i = O_2$.

From these circumstances, the volatilization rates of some contaminants on the actual water body can be estimated indirectly, according to Eq. 4, by using the data on $K_{V(env)}^{(O_2)}$:

$$K_{V(env)}^{(i)} = K_{V(env)}^{(O_2)} \times (K_V^{(i)}/K_V^{(O_2)}), \tag{4}$$

where $K_V^{(O_2)}$ is the oxygen-reaeration rate constant defined by Eq. 5 and where both $K_V^{(i)}$ and $K_V^{(O_2)}$ can be measured experimentally under well-defined conditions:

$$\mathrm{d}C^{(O_2)}/\mathrm{d}t = K_V^{(O_2)}(C_S^{(O_2)} - C^{(O_2)}), \tag{5}$$

where $C_S^{(O_2)}$ is the solubility of oxygen in water for a partial of oxygen in the atmosphere.

The volatilization rate of mercury in the actual water body has not been estimated, although mercury is one of the most important environmental contaminants and can be anticipated to volatilize readily to the atmosphere.4) In this work, the $K_V^{(i)}/K_V^{(O_2)}$ ratio, which is the determining factor for the volatility of the contaminants, was determined experimentally for mercury.

Experimental

All the chemicals used were of an analytical reagent grade. A schematic diagram of the experimental apparatus is shown in Fig. 1. The volatilization rate constant of mercury was measured as follows. An aqueous solution of mercury(II) chloride at the concentration of the ppb level (below the value of elemental mercury solubility17) in water) was prepared in the vessel (V in Fig. 1) and was then stirred at a constant agitation speed by means of a magnetic stirrer. The vessel was maintained at a constant temperature, and air was made to flow through the space above the aqueous solution in the vessel, the absorption cell(C), and the absorber(S),

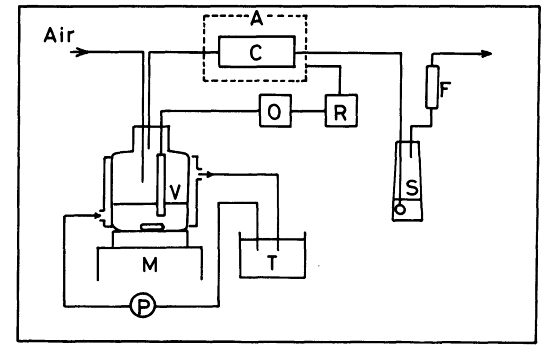

Fig. 1. Schematic diagram of apparatus.
A: Atomic absorption spectrophotometer, C: absorption cell, F: flow meter, M: magnetic stirrer, O: dissolved oxygen analyzer, P: pump, R: recorder, S: ($KMnO_4 + H_2SO_4$) absorber, T: thermostat, V: volatilization vessel.

successively, at a constant flow rate throughout the measurements. By the addition of hydrazine hydrate to the aqueous solution as a reducing agent,[4] the mercury(II) species were reduced quickly and completely to elemental mercury. The elemental mercury thus formed began immidiately to volatilize into the flowing air. The concentration of mercury in air was continuously measured from the absorbance at 253.7 nm obtained by means of an absorption spectrophotometer(A). The volatilization rate constant of mercury was determined by fitting the côncentration data to the integral form of Eq. 1.

As to the measurement of the oxygen-reaeration rate, the distilled water in the vessel(V) was purged with nitrogen to remove most of the dissolved oxygen. By agitating the water at a constant agitation speed, oxygen from the atmosphere was dissolved in the oxygen-deficient water. The oxygen-reaeration rate constant was determined by fitting the data of the oxygen concentration in the water, as measured by means of a dissolved oxygen analyzer, to the integral form of Eq. 5.

Results and Discussion

The volatilization rate constant of mercury, $K_v^{(Hg)}$, was unaffected by the mercury concentration over the range from 5×10^{-11} to 2.5×10^{-10} mol m^{-3}, as was to be expected from Eq. 2. The effect of turbulence in the gas phase on $K_v^{(Hg)}$ and on the oxygen-reaeration rate constant, $K_v^{(O_2)}$, was not observed over the air-flow rate range from 0.03 to 0.3 m^3 h^{-1} at 298 K, as shown in Fig.

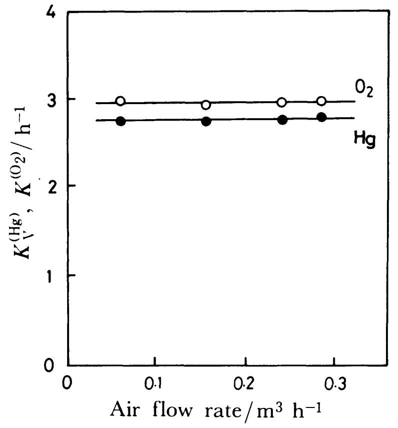

Fig. 2. Effect of air flow rate on $K_v^{(Hg)}$ and $K_v^{(O_2)}$ at 298 K.
Agitation speed: 320 min^{-1}, water depth: 3.7×10^{-2} m.

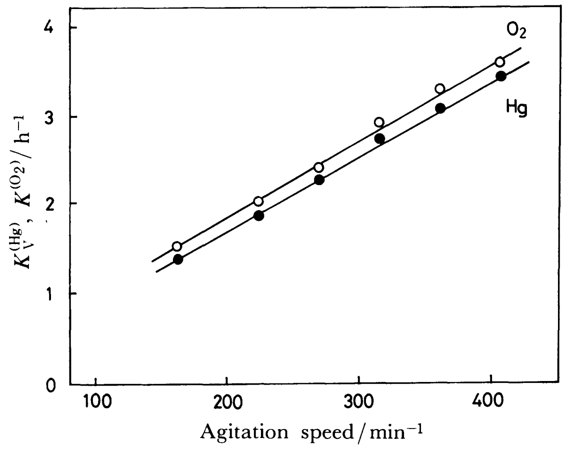

Fig. 3. Effect of agitation speed on $K_v^{(Hg)}$ and $K_v^{(O_2)}$ at 298 K.
Air flow rate: 0.24 m^3 h^{-1}, water depth: 3.7×10^{-2} m.

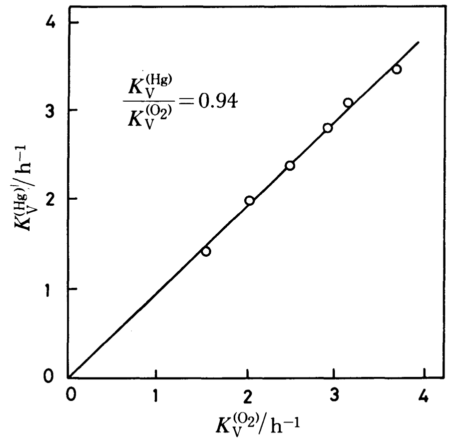

Fig. 4. Relation between $K_v^{(Hg)}$ and $K_v^{(O_2)}$ at 298 K.

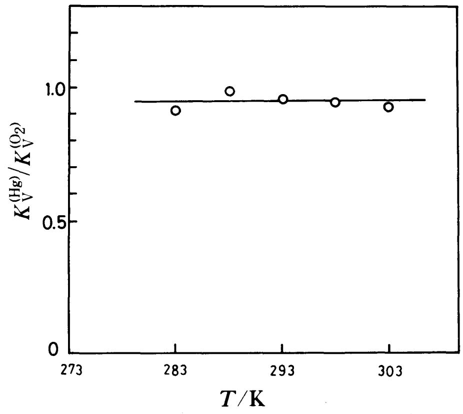

Fig. 5. Effect of temperature on $K_v^{(Hg)}/K_v^{(O_2)}$.
Air flow rate: 0.24 m^3 h^{-1}, water depth: 3.7×10^{-2} m, agitation speed: 320 min^{-1}.

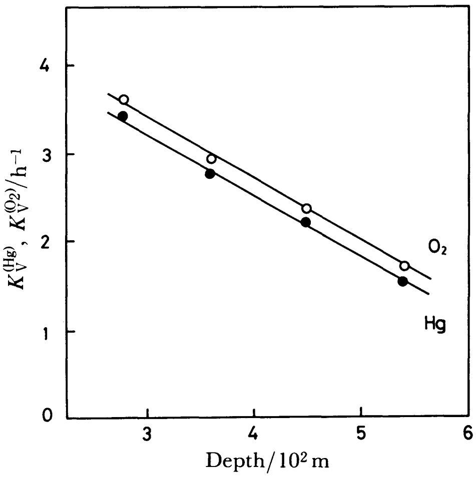

Fig. 6. Effect of water depth on $K_v^{(Hg)}$ and $K_v^{(O_2)}$ at 298 K.
Air flow rate: 0.24 m^3 h^{-1}, agitation speed: 320 min^{-1}.

Table 1. Volatilization rate constant and half-life of contaminants estimated as $K_{v(env)}^{(O_2)}=10^{-2}$ h^{-1}

Contaminant (i)	Molecular weight	$K_v^{(i)}/K_v^{(O_2)}$	$K_{v(env)}^{(i)}$/h^{-1}	$\tau^{(i)}$/d	Vapor pressure/Pa (at 298 K)
Mercury	200.59	0.94	9.4×10^{-3}	3.1	0.245
Benzene	78.11	0.56	5.6×10^{-3}	5.2	12700
Tetrachloroethylene	165.83	0.52	5.2×10^{-3}	5.6	2400

2. On the other hand, both the rate constants increased with an increase in the agitation rate in the aqueous phase, as shown in Fig. 3. From these data, the values of $K_v^{(Hg)}$ and $K_v^{(O_2)}$ at 298 K were related by a linear relationship with a slope of 0.94 ($=K_v^{(Hg)}/K_v^{(O_2)}$), as shown in Fig. 4. The $K_v^{(Hg)}/K_v^{(O_2)}$ ratio was observed to be independent of temperatures ranging from 283 to 303 K, as shown in Fig. 5, although both the rate constants increased with a rise in the temperatures. Figure 6 shows the effect of the depth of the solution on the rate constants, indicating that the greater the depth, the smaller the rate constants become at a constant agitation speed because of the smaller turbulence in the aqueous solution and the smaller interfacial area. However, the $K_v^{(Hg)}/K_v^{(O_2)}$ ratio did not change, regardless of the depth.

Mackay and Leinonen[5] have suggested that mass transfer in the liquid phase is rate-controlling when the value of Henry's law constant is greater than 500 m^3 Pa mol^{-1}. Henry's law constant of mercury and oxygen is 993[6] and 79240[7] m^3 Pa mol^{-1} respectively at 298 K. As has been mentioned above, the mercury-volatilization rate and the oxygen-reaeration rate were both much many affected by the turbulence in the liquid phase than by that in the gas phase; consequently, these results support the suggestion of Mackay and Leinonen. Therefore, most of the resistance to these mass-transfer rates is concluded to lie in the liquid-phase boundary layer; thus, the term of $(RT/H^{(i)})(1/k_G^{(i)})$ in Eq. 2 can be neglected.

Taking into account the fact that the mass-transfer coefficient is proportional to the n-th power of diffusivity,[8] together with the above consideration, Eq. 6 is obtained from Eq. 2:

$$K_v^{(Hg)}/K_v^{(O_2)} = K_L^{(Hg)}/K_L^{(O_2)} = (D_L^{(Hg)}/D_L^{(O_2)})^n, \tag{6}$$

where D_L is the diffusivity** in the liquid phase. The value of n is $0.5\leq n\leq 1$, where n becomes unity in the case based on the classical theory of the two-film mass-transfer model[9] and where n is equal to 0.5 according to the theories of the penetration model[10] or the surface-renewal model[11]. From Eq. 6, the value of $K_v^{(Hg)}/K_v^{(O_2)}$ is estimated to be 1.2 ($n=1$) or 1.1 ($n=0.5$) by using the Othmer-Thakar relation[12] of $D_L \propto V_b^{-0.6}$, where V_b is the molar volume at the boiling point, 0.83 ($n=1$) or 0.91 ($n=0.5$) by considering the inverse proportionality of D_L to the molecular diameter[13] and 1.3 ($m=-0.5$[14]) or 1.2 ($m=-0.31$[15]) by applying the relation of $K_v \propto V_c^m$, where V_c is the critical molar volume. Based on the Liss-Slater's relation[16] of $K_v \propto M^{-0.5}$, the value of 0.4 is obtained. Besides this, all the other estimated values are considered to support the value of 0.94 obtained experimentally in this work.

The values of the oxygen-reaeration rate constant in the representative environmental water bodies, $K_{v(env)}^{(O_2)}$ [h^{-1}], have been reported[1] to be 4.6×10^{-3}—9.6×10^{-3} for ponds, 4.2×10^{-3}—3.9×10^{-1} for rivers, and 4.2×10^{-3}—1.2×10^{-2} for lakes. Table 1 shows the $K_{v(env)}^{(i)}$ values calculated by Eq. 4 for some contaminants, taking the value of $K_{v(env)}^{(O_2)}$ to be 10^{-2} h^{-1} and the values of $K_v^{(i)}/K_v^{(O_2)}$ to be 0.94, 0.57,[7] and 0.52[7] for mercury (in this work), benzene, and tetrachloroethylene respectively. Table 1 also shows the half-life times of the contaminants, $\tau^{(i)}$, defined by Eq. 7:

$$\tau^{(i)} = \ln 2/K_{v(env)}^{(i)}. \tag{7}$$

As is apparent in Table 1, mercury volatilizes about 1.7—1.8 times more rapidly than benzene or tetrachloroethylene, although the latter has much higher vapor pressures and smaller molecular weights. In this work, it has been demonstrated that the volatiliation of mercury in a water body to the atmosphere occurs much faster than has generally been appreciated.

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** The diffusivity of mercury has not been measured.