Hg Absorption in Aqueous Permanganate

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Aqueous acidic permanganate is known to be an effective solvent for elemental Hg vapor (Monkman et al., 1956; Hara, 1975). EPA method 29 specifies permanganate as the scrubbing solution for determination of elemental mercury in gas streams (Environmental Protection Agency, 1992). Permanganate has been used to collect mercury in flue-gas field sampling procedures (Shendrikar et al., 1984). Even though permanganate is an expensive reagent, it is effective at low concentration for mercury removal, so it may be commercially useful for air-pollution control or removal of mercury from other gases. No previous work was found giving the rate of reaction of permanganate with mercury. Therefore, the objective of this study was to quantify the kinetics in a well-characterized gas-liquid contactor.

Experimental Method

All experiments were performed in a well-characterized stirred cell reactor. Shen and Rochelle (1995) used a similar reactor to measure NO_2 absorption in sulfite solutions. The liquid-phase mass-transfer coefficient of the reactor was determined by Hg and CO_2 desorption from water. The gas-phase mass-transfer coefficient was determined by Hg absorption into concentrated permanganate solution.

The cylindrical reactor had a 10-cm diameter and 16-cm height. The total volume of the reactor was 1.295 L. The volume of solution used in each experiment was 1.06 L. The gas-liquid contact area was 81 cm^2. The reactor vessel was a thick glass cylinder with Teflon coated 316 stainless steel plates sealed to the top and bottom by thick gasket clamps. Four 3/8-in. wide, equally-spaced, Teflon-coated, 316 stainless steel baffles were welded to the bottom plate. The bottom plate contained ports for liquid inlet and outlet. The top plate contained ports for the gas inlet and outlet, solution injection, and a pressure gage. The gas inlet was at the near center of the top plate, directly above the gas agitator blade, to ensure that the inlet gas was properly mixed. The reactor was equipped with Teflon-coated gas-phase and liquid-phase agitators which were independently controlled. The diameter of the gas and liquid agitators was 6.35 and 5.08 cm, respectively. The agitator speed was measured by a digital tachometer, and for most of the experiments the agitation speed for both gas and liquid phases was between 500 and 700 rpm. All the fittings and valves used in the system were made from Teflon or inert plastics. The experiments were performed at 25 and 55°C.

Synthetic flue gas was prepared by mixing a known amount of elemental Hg vapor with nitrogen to produce a constant flow rate of Hg vapor to the reactor. Mercury vapor was obtained from VICI Metronics Hg permeation tubes. The flow rate of all gas streams was maintained by Brooks mass-flow controllers. The mixture of Hg and nitrogen entered the reactor through the gas inlet on the top of the plate, and Hg vapor was absorbed across an unbroken interface into a well-mixed solution. Nitrogen was added to dilute the gas before and after the reactor by a factor of ten, respectively. Nitrogen dilution after the reactor minimized the effect of water vapor on Hg analysis by a cold vapor atomic absorption spectrophotometer (LDC Analytical, model 3200). Gas after the reactor was continuously analyzed for Hg. The rate of Hg absorption was calculated from the gas-phase material balance. A four point calibration was performed before and after each run to minimize the effect of base line drifting of the analyzer.

Stock solution of 0.1 M permanganate was prepared from $KMnO_4$ solid (EM Science), standardized by $Na_2C_2O_4$ (Baker Analyzed Reagent) titration and stored in a brown bottle. A known amount of the above permanganate solution or freshly prepared diluted permanganate solution was injected into 1.8 M sulfuric acid (EM Science). MnO_4^- concentration in the liquid phase was determined by weighing the syringe before and after the injection.

Theory of Mass Transfer with Simultaneous Chemical Reaction

The rate of reaction between Hg vapor and $KMnO_4$ is given by the mechanism

$$Hg + MnO_4^- \rightarrow \text{Products} \tag{1}$$

$$\text{reaction rate} = k_2[Hg]_i\,[MnO_4^-]_i \tag{2}$$

Using surface renewal theory (Danckwerts, 1970), the flux of Hg, N_{Hg}, should be given by

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Table 1. Physical Properties of Hg and MnO_4^-

	25°C	55°C
D_{Hg-H_2O}*$(cm^2 \cdot s^{-1})$	1.19×10^{-5}	2.21×10^{-5}
$D_{MnO_4^- H_2O}$**$(cm^2 \cdot s^{-1})$	1.63×10^{-5}	3.18×10^{-5}
H_{Hg}† $(atm \cdot M^{-1})$	8.91	35.64
$k_{g,Hg}$ $(mol \cdot s^{-1} \cdot atm^{-1} \cdot m^{-2})$	$0.0344(n_g)^{0.38}$	$0.0344(n_g)^{0.38}$
$k^\circ_{l,Hg}$ $(m \cdot s^{-1})$	$2.42 \times 10^{-7}(n_l)^{0.73}$	$7.64 \times 10^{-7}(n_l)^{0.64}$
k°_{l,MnO_4^-} $(m \cdot s^{-1})$	$2.83 \times 10^{-7}(n_l)^{0.73}$	$9.15 \times 10^{-7}(n_l)^{0.64}$

*Estimated using Sitaraman et al.'s eqn. (Sitaraman et al., 1963).
†Obtained from Clever et al. (1985).
**Obtained from Lide (1994).

$$N_{Hg} = \frac{P_{Hgi}}{H_{Hg}} \sqrt{k_2 \, [MnO_4^-]_i \, D_{Hg-H_2O}} \qquad (3)$$

where

$$P_{Hgi} = P_{Hgb} - \frac{N_{Hg}}{k_g} \qquad (4)$$

$$[MnO_4^-]_i = [MnO_4^-]_b - \frac{N_{Hg}}{k^\circ_{l,MnO_4^-}} \qquad (5)$$

The value of $k^\circ_{l,Hg}$ obtained from Hg desorption experiments in an identical reactor was modified to give $k^\circ_{,MnO_4^-}$

$$k^\circ_{l,MnO_4^-} = k^\circ_{l,Hg} \sqrt{\frac{D_{MnO_4^- - H_2O}}{D_{Hg-H_2O}}} \qquad (6)$$

The value of k_g is provided in detail in the next section (Eq. 7). All physical constants used in the calculation are tabulated in Table 1.

Results and Discussion

Table 2 gives the experimental results for Hg absorption. At 2.3 mM $KMnO_4$, the Hg removal is practically the same as with 0.6 mM $KMnO_4$. This indicates that the absorption of Hg into 2.3 mM $KMnO_4$ is gas-phase controlled, which leads to the measurement of the gas-phase mass-transfer coefficient. The results are tabulated in Table 3.

The obtained gas-phase mass-transfer coefficient of Hg in this reactor is

$$k_g A = 2.784 \times 10^{-4} \, (n_g)^{0.38} \qquad (7)$$

These kgA values are smaller than those measured by McGuire with SO_2 absorption into NaOH solution in an

Table 2. Effect of $KMnO_4$ on Hg Removal During Hg Absorption in $KMnO_4$/1.8M H_2SO_4 Solution (Total Hg/N_2 flow rate was 1 l/min)

T (°C)	P_{Hgin} $\times 10^8$ atm	P_{Hgb} $\times 10^8$ atm	N_{Hg} $\times 10^9$ $mol/s \cdot m^2$	$[MnO_4^-]_b$ mM	$k_{g,Hg}$ $mol/s \cdot atm \cdot m^2$	$k_l{}^\circ{}_{MnO_4^-}$ $\times 10^5$ m/s	k_2 $\times 10^{-7}$ l/M-s
25	2.0	1.5	0.4	0.003	0.4	3.2	1.4
25	2.0	1.4	0.5	0.008	0.4	3.2	1.5
25	2.0	1.3	0.6	0.014	0.4	3.3	1.5
25	2.0	1.1	0.8	0.034	0.4	3.3	1.5
25	2.0	1.0	0.9	0.061	0.4	3.3	1.5
25	2.0	0.8	1.0	0.168	0.4	3.3	1.5
25	9.9	8.0	1.6	0.002	0.4	3.2	1.4
25	9.9	4.4	4.7	0.093	0.4	3.2	1.5
25	10.0	7.3	2.5	0.007	0.4	3.2	1.3
25	10.0	6.8	3.0	0.011	0.4	3.2	1.5
25	10.0	6.2	3.5	0.019	0.4	3.2	1.5
25	10.0	5.4	4.2	0.040	0.4	3.2	1.5
25	10.0	4.6	4.9	0.094	0.4	3.2	1.5
25	10.0	3.8	5.7	0.242	0.4	3.2	1.5
25	10.0	3.2	6.2	0.612	0.4	3.2	1.4
25	9.9	5.4	3.9	0.033	0.4	3.3	1.6
25	9.9	5.4	3.9	0.035	0.4	3.3	1.5
55	10.0	6.4	2.8	0.012	0.4	5.5	11.8
55	10.0	6.0	3.1	0.017	0.4	5.5	12.6
55	10.0	5.4	3.6	0.029	0.4	5.5	12.6
55	10.0	4.9	4.0	0.049	0.4	5.5	12.6
55	10.0	4.2	4.5	0.102	0.4	5.5	12.6
55	10.0	3.5	5.1	0.247	0.4	5.5	12.9

Table 3. Calibration of Gas Phase Mass-Transfer Coefficient by Hg Absorption in 3 mM $KMnO_4$/1.8 M H_2SO_4 Solution at 25°C.

$P_{Hgb} \times 10^8$ atm	n_g rpm	$k_gA \times 10^3$ $mol \cdot s^{-1} \cdot atm^{-1}$	$k_gA \times 10^3$* $(mol \cdot s^{-1} \cdot atm^{-1})$
2.63	164.5	1.91	2.39
2.43	208.5	2.13	2.87
2.26	286.5	2.37	3.65
2.10	344	2.58	4.19
1.98	415	2.76	4.83
1.82	540	3.07	5.91
1.68	708	3.39	7.25
1.64	776	3.50	7.78
1.57	925	3.68	8.89

$H_{g_{in}}$ was 9.90×10^{-8} atm and total Hg/N_2 flow rate was 1 l/min.
*$k_gA_{,Hg}$ was obtained from k_gA, $_{SO_2}$ (McGuire, 1990), corrected using $k_gA_{,Hg} = k_gA_{,SO_2}\sqrt{\frac{D_{Hg-N_2}}{D_{SO_2-N_2}}}$, where $D_{Hg-N_2} = 0.126$ $cm^2 \cdot s^{-1}$ (Nakayama, 1968) and $D_{SO_2-N_2} = 0.130$ $cm^2 \cdot s^{-1}$ (Marrero and Mason, 1972) at 25°C.

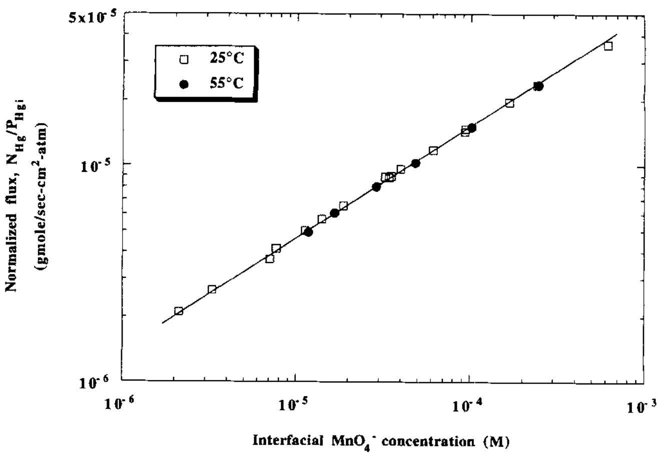

Figure 1. Dependence of normalized flux on $[MnO_4^-]_i$ during Hg absorption in $KMnO_4$/1.8 M H_2SO_4.
Total Hg/N_2 flow rate was 1 l/min..

identical reactor (McGuire, 1990), as shown in Table 3. McGuire (1990) showed that k_gA is independent of temperature from 25 to 55°C. We used the same k_gA correlation for both 25 and 55°C.

Table 2 also gives the results of Hg absorption into different concentrations of $KMnO_4$. It is obvious that Hg removal is responsive to the amount of MnO_4^- present in the solution. Figure 1 gives the dependence of normalized flux N_{Hg}/P_{Hgi} on the interfacial permanganate concentration $[MnO_4^-]_i$. These results are consistent with a reaction between Hg and MnO_4^- that is first order in MnO_4^-. For different inlet Hg concentration, all data were fit on one line, as shown in Figure 1. This indicates that the reaction is first order in Hg. The average value of the second-order rate constant k_2 $(M^{-1} \cdot s^{-1})$ is $(1.6 \pm 0.2) \times 10^7$ $M^{-1} \cdot s^{-1}$ at 25°C and $(12.6 \pm 5.3) \times 10^7$ $M^{-1} \cdot s^{-1}$ at 55°C at a 95% confidence level. The experimental data for k_2 were correlated with the following expression

$$k_2 = 1.018 \times 10^{17} \exp\left(\frac{-6{,}730}{T}\right) \tag{8}$$

The activation energy was calculated to be 56.0 kJ/mol (13.4 kcal/mol).

Other investigators studied the kinetics of MnO_4^- reaction with other reagents. Table 4 shows that the rate of permanganate reaction with mercury is faster than most reagents, but slower than reaction with hydrated electrons. The second-order reaction of elemental mercury and ozone was also reported with a rate constant of 4.7×10^7 $M^{-1}s^{-1}$ (Munthe, 1992), which was in the same order of magnitude but faster than mercury reaction with permanganate.

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Notation

A = gas-liquid contact area, m^2
$D_{Hg\text{-}H_2O}$ = liquid film diffusion coefficient of Hg, $m^2 \cdot s^{-1}$
$D_{MnO_4^- - H_2O}$ = liquid film diffusion coefficient of MnO_4^-, $m^2 \cdot s^{-1}$
D_{Hg-N_2} = interdiffusion coefficient of Hg and N_2, $m^2 \cdot s^{-1}$
$D_{SO_2-N_2}$ = interdiffusion coefficient of SO_2 and N_2, $m^2 \cdot s^{-1}$
H_{Hg} = Henry's constant of Hg, $atm \cdot M^{-1}$
$[H_g]_i$ = Hg concentration at the liquid side interface, M
k_2 = second-order rate constant, $M^{-1} \cdot s^{-1}$
k_g = gas film mass-transfer coefficient, $mol \cdot s^{-1} \cdot atm^{-1} \cdot m^{-2}$
$k^\circ_{l,\,Hg}$ = physical liquid film mass-transfer coefficient of Hg, $m \cdot s^{-1}$
k°_{l,MnO_4^-} = physical liquid film mass-transfer coefficient of MnO_4^-, $m \cdot s^{-1}$
$[MnO_4^-]_b$ = permanganate concentration in the bulk liquid phase, M
$[MnO_4^-]_i$ = permanganate concentration at the liquid side interface, M
n_g = gas-phase agitation speed, rpm
n_l = liquid-phase agitation speed, rpm
N_{Hg} = Hg flux, $mol \cdot s^{-1} \cdot m^{-2}$

Table 4. Second-Order Reaction Rate Constants of MnO_4^- with Different Reactants

Reactant	Medium	T(°C)	pH	$k_2(M^{-1} \cdot s^{-1})$	References
$[H_2Fe(CN)_6]^{2-}$	Na_3PO_3	15	2	5.2×10^5	Rawoof and Sutter (1967)
MnO_2 – Mn (adsorbed)	-	25	8	1.4×10^6	Benschoten and Lin (1992)
NO vapor	NaOH	25	-	4.4×10^6	Uchida et al. (1983)
H_2O radical	-	23	3	7.9×10^6	Baxendale et al. (1965)
Hg vapor	1.8M H_2SO_4	25	0	1.6×10^7	this work
Hg vapor	1.8M H_2SO_4	55	0	12.6×10^7	this work
Hydrated electron	MeOH	25	7	2.2×10^{10}	Thomas et al. (1964)
Hydrated electron	MeOH	25	13	3.7×10^{10}	Thomas et al. (1964)

$P_{\mathrm{Hg}b}$ = partial pressure of Hg in the bulk gas phase, atm
$P_{\mathrm{Hg}i}$ = partial pressure of Hg at the gas side interface, atm
$P_{\mathrm{Hg}in}$ = partial pressure of Hg in the inlet gas, atm
T = temperature, K

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