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The Disproportionation Constants of Mercurry(I) in Dilute Solutions. II[1]

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Synopsis. The equilibrium constants, K_d, of mercury(I) disproportionation have been measured by passing air containing mercury(0) vapor through mercury(I) solutions. At 15, 20, 25, 30, and 35 °C, the values of K_d were 1.3, 2.9, 5.2, 8.8, and 11×10^{-9} mol dm^{-3} respectively at $\mu = 0.1$ ($NaClO_4$).

In the preceding paper we have reported the equilibrium constants, K_d, for this reaction:[1]

$$\mathrm{Hg_2^{2+}} \rightleftharpoons \mathrm{Hg(aq)} + \mathrm{Hg^{2+}}. \tag{1}$$

The values of K_d we estimated are, however, considerably larger than those which have more recently been reported.[2] Our previous method of determining K_d may have caused some uncertainty in the absolute accuracy, so we have decided to reevaluate K_d by a modification of this earlier method.

The disproportionation occurs according to Reaction 1 by letting air flow through a solution containing Hg_2^{2+}, until finally only Hg^{2+} ions remain in the solution. Now, let us consider special conditions where the air introduced into the mercury(I) solution contains vapor of metallic mercury. Under such circumstances, the equilibrium of Reaction 1 will be attained depending on the dissolved Hg(aq) concentration. The K_d can be straightforwardly calculated by means of this equation:

$$\begin{aligned} K_d &= [\mathrm{Hg(aq)}][\mathrm{Hg^{2+}}]/[\mathrm{Hg_2^{2+}}] \\ &= [\mathrm{Hg(aq)}]\{[\mathrm{Hg^{2+}}]_0 + [\mathrm{Hg_2^{2+}}]_0 - [\mathrm{Hg_2^{2+}}]\}/[\mathrm{Hg_2^{2+}}], \end{aligned} \tag{2}$$

where the subscript 0 denotes the initial concentration.

The apparatus used is shown in Fig. 1. Air flowed by means of an air-pump P at a constant rate of 100 cm^3 min^{-1} through a cylindrical tube A, which was packed with silica gel, and a condenser B. The dried air was introduced into a flask C in which a few drops of metallic mercury had been put, and then bubbled successively into three flasks, D, E, and F. Finally, the air was released out of a cylindrical tube G in which a 1 mol dm^{-3} nitric acid solution had been placed in order to split off the contaminated mercury vapor. The flask C was maintained at a constant temperature below 10 °C by circulating thermostated water through a jacket outside the flask. The flasks, D, E, and F, were immersed in another thermostat controlled within 0.05 °C. In the E flask we placed a 100 cm^3 mercury(I) solution in 0.05 mol dm^{-3} perchloric acid, the ionic strength of which had been adjusted to 0.1 with sodium perchlorate. The same volumes of 0.05 mol dm^{-3} $HClO_4$ ($\mu = 0.1$, $NaClO_4$) solutions in the absence of mercury(I) were placed in the D and F flasks, which were utilized to estimate the [Hg(aq)] in the E flask. The dissolved Hg(aq) concentrations in the D and F flaks were determined by an atomic-absorption method, and the remaining Hg_2^{2+} concentrations in the E flask were measured spectrophotometrically at 236.5 nm; $[Hg_2^{2+}]_0 = 1.02 \times 10^{-5}$ mol dm^{-3} in all the runs.

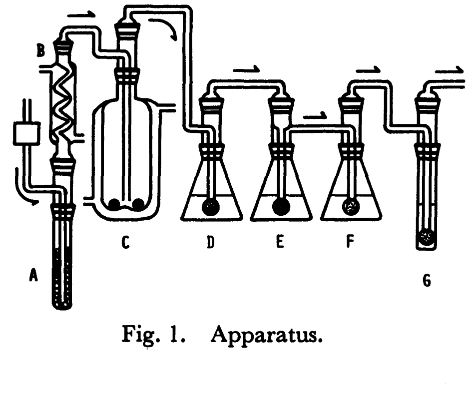

Fig. 1. Apparatus.

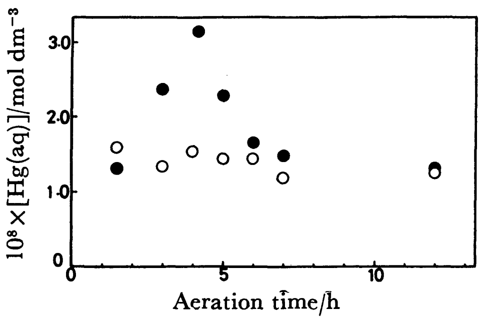

Fig. 2. Concentrations of Hg(aq) dissolved in D and F flasks as a function of aeration time. ○: D Flask, ●: F Flask. Temperature: 25.0 °C.

As will be seen in Fig. 2, the Hg(aq) concentrations in the D flask were almost constant, irrespective of the aeration time, while those in the F flask increased at first to attain a maximum and then decreased to approach those in the D flask. The initial increase in [Hg(aq)] in the postponed flask is due to the liberation of Hg^0 from mercury(I) in the E flask. We presumed that, when the [Hg(aq)] in the F flask was the same as that in the D flask, the [Hg(aq)] must be the same as in the E flask as well, and that, under such circumstances, the disproportionation equilibrium of mercury(I) in the E flask should be reached. After a 6-hour aeration, the amount of $[Hg_2^{2+}]$ remaining in the E flask and the mean values of [Hg(aq)] in the D and F flasks were used to calculate K_d by means of Eq. 2. The calculations were made by the successive approximation. That is, $[Hg^{2+}]_0$ was neglected as a first approximation, then, by using the approximate K_d value, $[Hg^{2+}]_0$ was estimated. It corresponded in most cases to *ca.* 10% of $\{[Hg_2^{2+}]_0 - [Hg_2^{2+}]\}$. Next, by using the $[Hg^{2+}]_0$ estimated, the second K_d value was calculated; it was no longer changed by further successive calculations.

The summary of the experimental results and the estimated disproportionation constants are listed in Table 1. The present result, 5.2×10^{-9} mol dm^{-3} at 25 °C, is in good agreement with that of the literature:

Table 1. Summary of experimental results and disproportionation constants estimated

Temp	$10^8\times$[Hg(aq)] mol dm^{-3}		$10^6\times[Hg_2^{2+}]^{c)}$	$10^9\times K_d$ mol dm^{-3}	
°C	Flask D	Flask F	mol dm^{-3}	a)	b)
15.0	0.686	0.686	8.8	1.1	1.2
	0.933	0.909	8.9	1.3	1.4
				Average	1.3
20.0	1.19	1.24	8.6	2.3	2.6
	1.45	1.61	8.7	2.6	3.0
	1.52	1.52	8.7	2.6	3.0
				Average	2.9
25.0	1.24	1.31	7.4	4.8	5.2
	1.09	1.09	7.1	4.8	5.1
				Average	5.2
30.0	1.43	1.65	6.5	8.8	9.5
	1.37	1.55	6.5	8.3	8.9
	1.28	1.34	6.5	7.5	8.1
				Average	8.8
35.0	1.48	1.64	6.3	9.7	10
	1.54	1.61	5.8	12	13
	0.92	1.05	5.1	9.9	10
				Average	11

a) First approximation by neglecting $[Hg^{2+}]_0$. b) The corrected K_d. c) $[Hg_2^{2+}]_0 = 1.02\times10^{-5}$ mol dm^{-3} in all runs.

$3.0^{2)}$ and $5.3^{3)}\times10^{-9}$ mol dm^{-3} at 25 °C. Our previous results, which are two to four times larger than those obtained in the present work, are considered to be less reliable. In the previous method, we estimated K_d by combining two rate constants determined by separate experiments; one was concerned with Hg^0 transfer from the aqueous to the gaseous phase, and the other, with the disproportionation of mercury(I).$^{1)}$ The additional errors of the two rate constants may be responsible for the lesser reliability.

In general, the reliability of the method of determining K_d depends on how accurately it can determine the concentration of Hg(aq), which is in equilibrium with Hg_2^{2+} and Hg^{2+} ions. In this respect, several attempts that make use of the characteristic distribution of Hg^0 between aqueous and non-aqueous phases$^{3)}$ or between aqueous and gaseous phases$^{2)}$ have been made. We assume in the present method that the solubilities of Hg^0 in aqueous solutions in the presence of Hg_2^{2+} and Hg^{2+} ions are identical with those in their absence under the same vapor pressure of metallic mercury. It should be noticed that the concentration of Hg(aq) in each run is not a saturated solubility, but a so-called steady-state solubility. That is, mercury vapor continuously supplies Hg^0 to an aqueous phase, while the air stream bubbled out of the solution removes the dissolved Hg(aq) at a certain rate.

The total mercury concentrations in the D and F flasks, which can be measured by the atomic-absorption technique by using a tin(II) reductant, did not increase after more than a 10-hour aeration. We concluded, therefore, that the air-oxidation of the dissolved Hg^0 in 0.05 mol dm^{-3} $HClO_4$ solutions did not occur during the aeration. This is why we used air instead of nitrogen gas.

From the temperature dependence of K_d, the ΔH and ΔS values for Reaction 1 were found to be 79 kJ mol^{-1} and 108 J mol^{-1}K^{-1} at 25 °C.

References

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