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The Disproportionation Constants of Mercury(I) in Dilute Solutions

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The disproportionation constants for the $Hg_2^{2+} \rightleftharpoons Hg(aq) + Hg^{2+}$ reaction have been measured in dilute mercury(I) perchlorate solutions over the temperature range from 15 to 30 °C. The technique was based on a simple kinetic method which made use of a characteristic property of the elemental mercury in aqueous solutions. The disproportionation constant at 25 °C and $\mu = 0.1$ was found to be $1.1 \pm 0.1 \times 10^{-8}$ M, and the associated thermodynamic parameters were $\Delta H = 13.2 \pm 0.2$ kcal/mol and $\Delta S = 8.0 \pm 0.8$ e.u. The reliability of the method was discussed with relation to the reported values in the literature.

It is widely accepted that mercury(I) ions in aqueous solutions exist in the dimeric form and are in equilibrium with dissolved mercury atoms and mercury(II) ions, and that the equilibrium is rapidly established:[1,2]

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

The equilibrium constant, K_d, can be expressed by $K_d = [Hg^{2+}]f_2 \cdot [Hg(aq)]f_0/[Hg_2^{2+}]f_1$, where the brackets indicate molarities and where the f values are activty coefficients for the corresponding species. It has been common practice to assume that $f_0 = 1$ and that $f_2 = f_1$, an approximation which is reasonable at low ionic strengths. Therefore, the equilibrium constant can be expressed more conveniently by

$$K_d = [Hg^{2+}][Hg(aq)]/[Hg_2^{2+}]. \tag{2}$$

Kinetic and thermodynamic studies of the reactions concerned with mercury(I) require accurate knowledge of the disproportionation constant.[2-7] Potentiometric studies of $[Hg^{2+}]/[Hg_2^{2+}]$ ratios have been reported in the literature by many investigators.[8-11] However, there have been few studies of the equilibrium constant involving the [Hg(aq)] term, K_d. The first and the only attempt to determine the K_d was made by Moser and Voigt.[12] They made use of the extraction of free mercury into non-polar solvents to measure the extent of the disproportionation of mercury(I) and estimated K_d by using the solubilities of Hg^0 in an aqueous solution and organic solvents. The technique they used was, however, troublesome, and their data were limited to those at 25 °C.

This paper will describe a simple technique that might allow an estimation of the disproportionation constant of mercury(I) in dilute aqueous solutions. It makes use of the fact that elemental mercury in the aqueous phase is readily carried by an air-stream into the gaseous phase:

$$Hg(aq) \xrightarrow{k} Hg(gas), \tag{3}$$

where k is the rate constant associated with the Hg^0 phase-transfer. When a nitrogen gas is made to flow through a solution containing Hg_2^{2+}, the dispropotionation of mercury(I) may occur according to Reaction 1. Considering Process 3 to be a rate-controlling step, the rate of the disproportionation of mercury(I) can be expressed by:

$$-d[Hg_2^{2+}]/dt = kK_d[Hg_2^{2+}]/[Hg^{2+}]. \tag{4}$$

The initial concentration of Hg^{2+} in equilibrium with Hg_2^{2+} is sufficiently low, and $[Hg^{2+}] = [Hg^{2+}]_0 + [Hg_2^{2+}]_0 - [Hg_2^{2+}] = [Hg_2^{2+}]_0 - [Hg_2^{2+}]$. Then, Eq. 4 becomes, on integration

$$[Hg_2^{2+}]_0 \log [Hg_2^{2+}] - [Hg_2^{2+}]/2.303 = -kK_dt/2.303$$
$$+ [Hg_2^{2+}]_0 \log [Hg_2^{2+}]_0 - [Hg_2^{2+}]_0/2.303, \tag{5}$$

where the subscript 0 denotes the initial concentration. The rate constant, k, can be determined by a separate experiment. Nitrogen gas is passed through a solution containing a known concentration of elemental mercury, which can be prepared by saturating mercury vapor in an aqueous solution.[13] Then, Reaction 3 proceeds; its rate can be expressed by

$$-d[Hg(aq)]/dt = k[Hg(aq)], \tag{6}$$

which becomes, on integration

$$\log [Hg(aq)] - \log [Hg(aq)]_0 = -kt/2.303. \tag{7}$$

Eqs. 5 and 7 enable us to determine kK_d and k respectively, from which we can determine K_d.

Experimental

Reagents. Doubly distilled water was used throughout this work. All the chemicals were of an analytical reagent grade. The metallic mercury was purified in the usual manner.[13] The sodium perchlorate solutions to maitain a constant ionic strength were obtained by mixing sodium carbonate solutions and perchloric acid. The preparation and standardization of mercury(I) perchlorate solutions were all done in the way described in a previous paper.[3] Saturated solutions of elemental mercury of a constant ionic strength adjusted with $NaClO_4$ were prepared using a mercury-vapor solubility apparatus as has been described in a previous paper,[13] with a modification of its gas-inlet-type adaptor. A fritted disk was employed in place of the inlet glass tube in order to attain equilibrium within a shorter time. As a result of this modification, a time of 10 min was found to be sufficient to attain the solubility equilibrium.

Apparatus and Procedure. Two separate measurements were made: atomic absorption spectrophotometric measurements of elemental mercury, which lead to k values (*Procedure A*), and spectrophotometric measurements of mercury(I), which lead to kK_d values (*Procedure B*). Several Pyrex Erlenmeyer flasks of a 100-ml capacity and of the same size and form were used as reaction vessels in both *Procedures A* and *B*. The reaction vessel was connected at the ground-glass joint to a gas-washing-type adaptor. The adaptor was equipped with a fine tip of a glass tube *ca.* 1 mm i.d., and the front was positioned centrally 1 cm above the bottom of the reaction vessel. The reaction vessel containing the sample solution was immersed in a constant bath thermostated to within 0.05 °C.

Procedure A: A 40-ml portion of a saturated mercury solution was introduced into the reaction vessel. Then, nitrogen gas was immediately dispersed at a constant flow rate through the solution by means of the fine tip. The resulting mercury vapor was carried with the nitrogen stream through a 10-cm-path-length absorption cell with quartz windows, where it was detected by a Hitachi Model 508 atomic absorption spectrophotometer. In order to catch water droplets, an empty trap immersed in an ice-cooled bath was inserted between the reaction vessel and the cell. The absorption peaks of mercury were recorded on a Hitachi Model 108 recorder with a chart speed of 40 mm/min.

Procedure B: A 500-ml mercury(I) perchlorate solution was prepared by diluting a 10^{-3} M mercury(I) stock solution with 0.05 M $HClO_4$ and by adding a suitable volume of a 1 M $NaClO_4$ solution. This solution was then divided into 40-ml portions in separate reaction vessels which had been stoppered until used. Nitrogen gas was then passed through the solution under the same conditions as in *Procedure A*. After a fixed time, the reaction vassel was placed by another one. The solutions were measured by means of a Hitachi Model 181 spectrophotometer at 236.5 nm, and the concentrations of Hg_2^{2+} were determined based on a calibration curve.[14]

Results

Some typical results of atomic absorption monitoring of the elemental mercury carried with nitrogen gas at a constant flow rate are shown in Fig. 1. The ordinate is an arbitrary unit represented by the height on the recorder chart. The total peak area from zero to infinity time corresponds to the initial amount of mercury present in the solution, and is related to $[Hg(aq)]_0$, which can be predicted from the solubility study.[13] Then, we can estimate [Hg(aq)] at any time, t, by subtracting the peak area from zero to time t from the total peak area. As a matter of convenience, the summation of all the individual peak heights read every 1 mm on the abscissa is employed instead of the peak area. The plots of log[Hg(aq)] *vs.* t were found to be linear for at least 3 half-lives, as predicted from Eq. 7 in the range of the nitrogen flow rate from 1.5 to 2.5 l/min. A typical result is shown in Fig. 2. From the slope of the straight line, k was obtained. According to Eq. 5, the concentrations of Hg_2^{2+} were plotted against time t. The results are shown in Fig. 3. From the slope of the straight line, we can estimate the kK_d value.

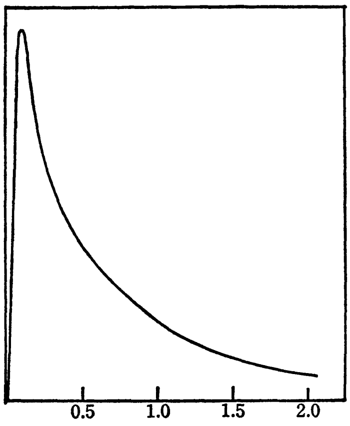

Fig. 1. Typical result of monitoring Hg° by atomic absorption spectrophotometry. The ordinate is an arbitrary unit represented by the recorder chart height. $[Hg(aq)]_0$; 1.75×10^{-7} M, temp; 15 °C, μ; 0.1, N_2 flow rate; 2.0 l/min.

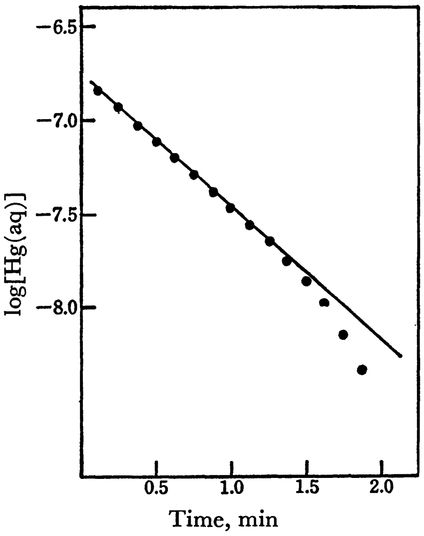

Fig. 2. Plot of Figure 1 according to Eq. 7.

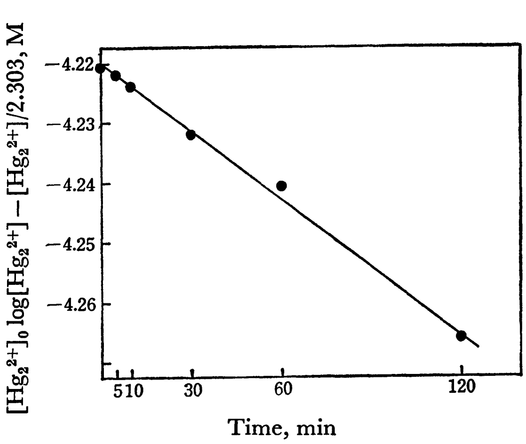

Fig. 3. Plot according to Eq. 5. $[Hg_2^{2+}]_0$; 0.76×10^{-5} M, temp; 15 °C, μ; 0.1, N_2 flow rate; 2.0 l/min.

The conditions under which some typical runs were made and their results are given in Table 1. The disproportionation constants of mercury(I) over the temperature range of 15 to 35 °C were determined under such conditions that $\mu=0.1$, nitrogen flow rate= 2.0 l/min, $[Hg_2^{2+}]_0=0.76\times10^{-5}$ M, and $[Hg(aq)]_0=$ saturated at each temperature under study. The results are listed in Table 2. The thermodynamic parameters associated with K_d are calculated from Table 2 by the least-squares method, $\Delta H=13.2\pm0.2$ kcal/mol and $\Delta S=8.0\pm0.8$ e.u.

Discussion

The method described here to determine the disproportionation constant of mercury(I) is essentially the

TABLE 1. THE EFFECTS OF THE IONIC STRENGTH, THE NITROGEN FLOW RATE, AND THE INITIAL CONCENTRATIONS OF Hg_2^+ AND Hg(aq) ON THE ESTIMATIONS OF k, kK_d, AND K_d

	k, min^{-1}	kK_d, 10^{-9} M min^{-1}	K_d, 10^{-9} M
Ionic strength (μ)	(N_2 flow rate; 2.0 l/min, temp; 15 °C, $[Hg_2^{2+}]_0$; 0.76×10^{-5} M, $[Hg(aq)]_0$; 1.75×10^{-7} M)		
0.05	1.6 ± 0.1	8.4 ± 0.8	5.2 ± 0.2
0.1	1.7 ± 0.1	8.2 ± 0.5	4.8 ± 0.1
N_2 flow rate (l/min)	(μ; 0.1, temp; 15 °C, $[Hg_2^{2+}]$; 0.76×10^{-5} M, $[Hg(aq)]_0$; 1.75×10^{-7} M)		
2.5	1.8 ± 0.1	9.2 ± 0.4	5.1 ± 0.1
2.0	1.7 ± 0.1	8.2 ± 0.5	4.8 ± 0.1
1.5	1.5 ± 0.1	8.4 ± 0.2	5.6 ± 0.2
$[Hg_2^{2+}]_0$, 10^{-5} M	(N_2 flow rate; 2.0 l/min, μ; 0.1, temp; 25 °C)		
1.52		21 ± 1	
0.76		23 ± 2	
0.38		22 ± 1	
$[Hg(aq)]_0$, 10^{-7} M	(N_2 flow rate; 2.0 l/min, μ; 0.1, temp; 25 °C)		
3.2	2.2 ± 0.1		
1.6	2.2 ± 0.1		
1.1	2.1 ± 0.1		

TABLE 2. DISPROPORTIONATION CONSTANTS DETERMINED AT VARIOUS TEMPERATURES[a)]

Temp, °C	k, min^{-1}	kK_d, 10^{-9} M min^{-1}	K_d, 10^{-9} M
15	1.7 ± 0.1	8.2 ± 0.5	4.8 ± 0.1
20	2.0 ± 0.1	16 ± 1	7.9 ± 0.1
25	2.2 ± 0.1	23 ± 2	11 ± 1
30	2.3 ± 0.1	36 ± 1	16 ± 1
35	2.5 ± 0.1	55 ± 1	22 ± 1

a) N_2 flow rate; 2.0 l/min, μ; 0.1, $[Hg_2^{2+}]_0$; 0.76×10^{-5} M, $[Hg(aq)]_0$; saturated at each temperature.

same as those used in the kinetic studies of oxidation reactions of mercury(I) with inorganic oxidants.[5)] According to Sykes and his co-workers,[6,15)] for two-equivalent oxidants with relatively low oxidation potentials, the general rate law is expressed satisfactorily by

$$-d[Hg_2^{2+}]/dt = k_1K_d[Hg_2^{2+}][\text{Oxidant}]/[Hg^{2+}]. \qquad (8)$$

The mechanism has been explained as involving the following paths:

$$Hg_2^{2+} \overset{K_d}{\rightleftarrows} Hg(aq) + Hg^{2+}, \text{ fast}$$

$$Hg(aq) + \text{Oxidant}(2e^-) \xrightarrow{k_1} Hg^{2+}$$

It is usually difficult to determine k_1 independently because of the limited solubility of elemental mercury in an aqueous solution. Therefore, the rate constant of the rate-controlling step, k_1, has been estimated by combining the observed rate constant and the K_d value.[5)] In the present study, Hg(aq), which is in equilibrium with Hg^{2+} and Hg_2^{2+}, was removed from the aqueous phase by the use of an inert gas instead of oxidants. In such a treatment, the reaction system is very much simplified, and, moreover, the rate constant in the rate-controlling step can be determined independently by the use of a highly sensitive atomic-absorption technique. The rate of Hg^0 transfer from the aqueous to the gaseous phase was taken to be the rate-controlling step because the disproportionation equilibrium is rapidly established. In such a heterogeneous system, the rate constant, k, must be a function of the surface area of the gaseous phase in contact with a solution, which depends on many factors, such as the shape of the nitrogen-inducing tube and the reaction vessel, the flow rate of the nitrogen gas, and the size of the sample solutions. However, the k required for the present purpose is not an inherent value, but a relative value sensitive only to the solution temperature. It is absolutely essential to carry out independent determinations of k under the same conditions as the determinations of kK_d. Under the present experimental conditions, N_2 flow rates in the range from 1.5 to 2.5 l/min were suitable for the determinations of k. Deviations from linear plots according to Eq. 7 were observed both at lower and higher flow rates than this range. These deviations are probably because a lower flow rate may result in an insufficient stirring of the aqueous phase, while a higher flow rate may result in the disturbance of a regular stream of the gaseous phase along the path from the reaction vessel and in the measuring cell. The variations in the initial concentrations of Hg_2^{2+}, 1.52×10^{-5} to 0.38×10^{-5} M, and Hg(aq), 3.2×10^{-7} to 1.1×10^{-7} M, have little effect on kK_d and k respectively, as may be seen from Table 1. This appears to support the rate laws expressed by Eqs. 4 and 6.

The present method is very similar to that by Moser and Voigt,[12)] though different experimental approaches are employed, that is, a kinetic and a static method respectively. The latter requires accurate solubility data of elemental mercury in water and organic solvents, while the present kinetic method does not require the absolute values of $[Hg_2^{2+}]$ and $[Hg(aq)]$, since they have no effects on the slopes of the rate plots obtained by means of Eqs. 5 and 7. The K_d value at 25 °C determined in the present study is about two times larger than that reported by Moser and Voigt, 5.5×10^{-9} M. The discrepancy, however, seems to be small when we consider the different experimental approaches employed in the two studies.

The thermodynamic principles underlying the Hg(0)/Hg(I)/Hg(II) equilibria are quite well understood. The equilibrium constant, $K=[Hg^{2+}]/[Hg_2^{2+}]$, can be calculated from the formal potentials of the Hg(I)-Hg(0) and Hg(II)-Hg(I) couples reported in the literature, ranging from 0.006 to 0.012.[7,12,16] The product of K and the mercury solubility, 3.2×10^{-7} M,[13] comes to be from 1.9×10^{-9} to 3.8×10^{-9} M. The potentiometric method may give a reliable K value in the presence of liquid mercury. However, it appears extremely doubtful that the product of K and the mercury solubility should be taken as K_d. The solubility of mercury cited in the literature might be unsuitable for predicting [Hg(aq)] under relatively high mercury(I) concentrations and in the presence of liquid mercury because of the formation of the colloidal mercury.[17] If the colloidal mercury could take part in the disproportionation equilibrium, Reaction 1 should be shifted to the left, leading to a lower apparent K_d. In the studies of reactions concerned with dilute mercury(I) ions in which mercury atoms are present in equilibrium with Hg_2^{2+} and Hg^{2+} and are not in excess, the K_d value should be adopted as the equilibrium constant.

Schwarzenbach and Anderegg have reported that, for the $Hg(l)+Hg^{2+}\rightleftharpoons Hg_2^{2+}$ reaction, $\Delta H°=-0.820$ kcal/mol, $\Delta S°=6.0$ e.u., and $\Delta G°=-2.62$ kcal/mol.[10] In the present study, $\Delta H°=13.2$ kcal/mol, $\Delta S°=8.0$ e.u., and $\Delta G°=10.8$ kcal/mol were obtained for the $Hg_2^{2+}\rightleftharpoons Hg(aq)+Hg^{2+}$ reaction. When these two reactions are compared, it follows that $\Delta G°=8.19$ kcal/mol for the $Hg(l)\rightleftharpoons Hg(aq)$ equilibrium. A termodynamic datum for this equilibrium has been published: $\Delta G°=9.4$ kcal/mol.[18] The discrepancy between these two values may be partly due to the experimental errors.

In his spectrophotometric study Higginson suggested a homolytic dissociation, $Hg_2^{2+}\rightleftharpoons 2\,Hg^+$, in dilute mercury(I) solutions and reported a value of $k_{diss}=[Hg^+]^2/[Hg_2^{2+}]$ within the limits of 10^{-8} and 10^{-6} M.[14] However, such a dissociation constant was not taken into consideration in the present work for the following reasons, as suggested by other investigators: (1) a deviation from Beer's law in dilute mercury(I) solutions was not observed by another investigator;[19] (2) a K_{diss} value as large as 10^{-7} M is shown by the extraction technique to be highly unlikely[12] and (3) the evidence for a contribution from $[Hg_2^{2+}]^{1/2}$ instead of $[Hg_2^{2+}]$ has not been observed in kinetic studies of the reactions in which mercury(I) ions are concerned.[6]

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