

Electrometric Investigation of Equilibria between Mercury and Halogen Ions. VIII. Survey and Conclusions

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In the seven preceding publications¹⁻⁷ the work of a team investigating the equilibria between Hg^{2+} and the halogen ions Cl^- , Br^- , and I^- has been described. Now that the work is concluded for the time being, it seems appropriate to collect the main results and to try to visualize them in the form of diagrams.

SURVEY OF PARTS I—VII

A review of previous work on mercury-halogen complexes showed that a new investigation was desirable for many reasons, *e. g.* the equilibria involving Hg^{2+} — HgX^+ — HgX_2 have as far as we know not been investigated since 1908. On the equilibria involving HgX_2 — HgX_3^- — HgX_4^{2-} somewhat more work has been done. However, the investigators of the latter equilibria can be divided into two groups. Some have assumed that only HgX_3^- appears in appreciable amounts, and neglected HgX_4^{2-} . The others have, on the contrary, neglected HgX_3^- and assumed that only HgX_4^{2-} is formed.

Moreover the influence of acidity and ionic strength on these equilibria, which can be expected to be rather great, has as a rule been neglected.

It was decided to study the Hg^{2+} -halogen equilibria at 25° C by electrometric methods, using solutions of constant acidity (10 mC) and with ionic strength as constant as possible (500 mC), using NaClO_4 as salt medium. In this way the activity factors were kept approximately constant; otherwise the calculations would have been hopelessly complicated.

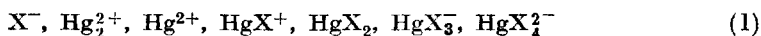
At high concentrations $[\text{Br}^-]$ and $[\text{I}^-]$ it was possible to measure the concentration of free Hg^{2+} , using a Hg electrode (Parts VI and VII). In no other

instance, however, was it possible to measure the concentrations $[\text{Hg}^{2+}]$ or $[\text{X}^-]$ directly, using electrodes of the first or second kind. Instead indirect methods must be used. A large part of our investigations was founded on measurements of redox emfs using solutions with both Hg_2^{2+} and Hg^{2+} , generally in equilibrium with solid Hg_2X_2 . For interpreting these emfs it was necessary also to know the solubility products of the mercury(I)halides, Hg_2X_2 , under the special conditions of our work.

In Part I earlier work is reviewed, the general plan of the work is given, and the apparatus and analytical methods are described. Part II describes measurements of the equilibria $\text{Hg}^{2+} + \text{HgX}_2 \rightleftharpoons 2\text{HgX}^+$ (the value given for I^- is only preliminary). Part III deals with measurements of the solubility products for the Hg_2X_2 , and of the equilibrium $\text{Hg}^{2+} + \text{Hg}(1) \rightleftharpoons \text{Hg}_2^{2+}$. Part IV is theoretical and gives the formulae for the variation of the redox emf, when halogen ions X^- are added to a $\text{Hg}_2^{2+} - \text{Hg}^{2+}$ mixture. The equilibria are rather complicated, since solid Hg_2X_2 appears in addition to the various $\text{Hg}^{2+} - \text{X}^-$ complexes. Finally, parts V—VII deal with the measurements for the individual halogens, Cl^- (part V), Br^- (part VI), and I^- (part VII). For no two halide systems has it been possible to use exactly the same experimental and computational methods, because of the great differences between the equilibrium constants for Cl^- , Br^- , and I^- .

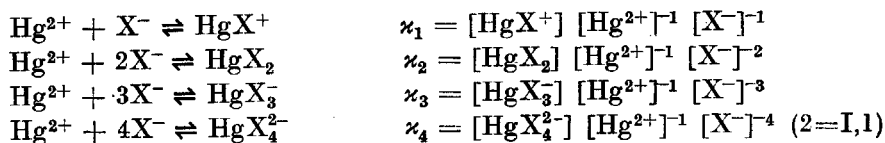
EQUILIBRIUM CONSTANTS

Our measurements could be explained assuming that the following molecular species, and only these, appear in the solutions:

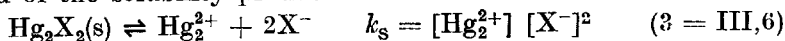


It was not possible to neglect the existence of any one of the $\text{Hg}^{2+} - \text{X}^-$ complexes. On the other hand there was no need to assume that, for instance, univalent mercury also forms single ions Hg^+ or soluble complexes Hg_2X^+ , or that there are higher complexes of bivalent mercury such as HgX_5^{2-} and HgX_6^{4-} or polynuclear complexes such as Hg_2X_5^- , $\text{Hg}_3\text{X}_8^{2-}$, and the like. This is not to deny the presence of a few of these molecular species in small amounts, or even in considerable amounts under special conditions; thus it is possible that polynuclear Hg^{II} complexes may appear at higher total Hg^{II} concentrations than those used by us, which were generally ≤ 10 mC.

The most concise way of giving our results is a table of the complex products $\kappa_1 - \kappa_4$, defined by



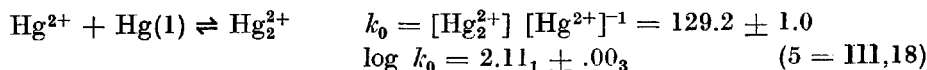
and of the solubility products



The logarithms of these quantities for Cl^- , Br^- , and I^- (on the C scale) are listed below:

	X = Cl	Br	I	
log κ_1	6.74 ± .02	9.05 ± .03	12.87 ± .03	
log κ_2	13.22 ± .02	17.33 ± .04	23.82 ± .04	
log κ_3	14.07 ± .15	19.74 ± .11	27.60 ± .14	
log κ_4	15.07 ± .06	21.00 ± .03	29.83 ± .02	
log k_s	-16.88 ± .01	-21.29 ± .04	-27.47 ± .01	(4)

Together with the equilibrium constant k_0 :



and the solubility of HgI_2 according to Biedermann and Sillén⁶:

$$s = (7.4 \pm .3) \cdot 10^{-5} \text{ C}; \log s = -4.13 \pm 0.02 \quad (6)$$

these constants permit the calculation for each halogen of all equilibria involving the above mentioned molecular species (1) in solution, Hg metal, and solid Hg_2X_2 (for I also solid HgI_2).

DISTRIBUTION OVER DIFFERENT COMPLEXES

Since it may be difficult to grasp immediately the significance of these figures, we have tried to illustrate them by means of diagrams.

Figs. 1 a—c have as abscissa the logarithm of the concentration of free halogen ions, Cl^- , Br^- , or I^- . The ordinate goes from 0 to 100 and shows the percentage of the total amount of Hg^{II} present in the form of different com-

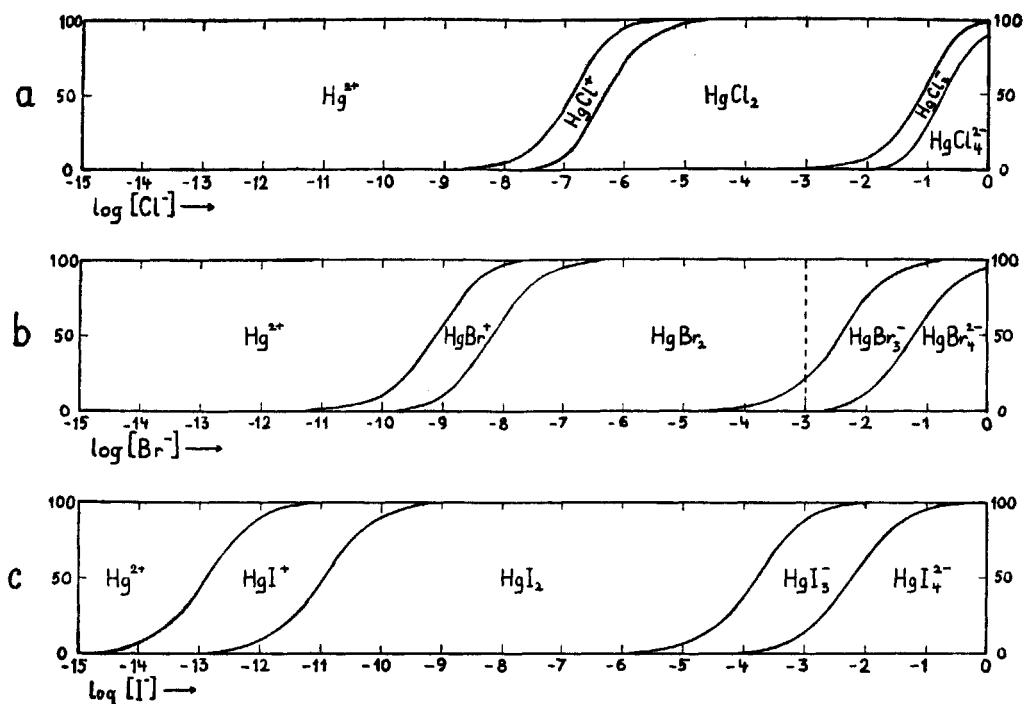


Fig. 1. Distribution of Hg^{II} over different complexes with a) Cl^- b) Br^- c) I^- for varying $[\text{X}^-]$. The abscissa is $\log [\text{X}^-]$. On the ordinate axis the distance 0—100 represents the total amount of Hg^{II} present. If for a given value of $[\text{X}^-]$, a vertical line is drawn at the corresponding $\log [\text{X}^-]$, the segment of this line falling in a certain area, e. g. HgX_3 , represents the fraction of the total amount of Hg^{II} present as that complex.

plexes at the $[\text{X}^-]$ given. For example, we see that in a bromide solution containing 1 mC free Br^- ($\log [\text{Br}^-] = -3$, dotted line in Fig. 1b) about 20 % of all Hg^{II} is present as HgBr_3^- , and about 80 % as HgBr_2 ; other complexes are negligible. With 10 mC free Br^- ($\log [\text{Br}^-] = -2$), about 12 % of all Hg^{II} is present as HgBr_4^{2-} , about 63 % as HgBr_3^- , and about 25 % as HgBr_2 . At higher $[\text{Br}^-]$, HgBr_4^{2-} becomes the predominant complex. Between $[\text{Br}^-] = 10^{-4}$ and 10^{-7} , there is a broad range with HgBr_2 dominating. At lower $[\text{Br}^-]$, the amounts of HgBr^+ and Hg^{2+} become considerable. At $[\text{Br}^-] = 10^{-9}$, we have, for instance, 9 % HgBr_2 , 48 % HgBr^+ , and 43 % Hg^{2+} . Below $[\text{Br}^-] = 10^{-11}$ C practically only Hg^{2+} is present.

These percentages must be independent of the total concentration of Hg^{II} , as can be seen from the formulae used for the derivation of the curves.

According to (2), denoting (X^-) by X



$$\begin{aligned} \text{Thus } [\text{Hg}^{\text{II}}]_{\text{total}} &= [\text{Hg}^{2+}] + [\text{HgX}^+] + [\text{HgX}_2] + [\text{HgX}_3^-] + [\text{HgX}_4^{2-}] = \\ &= [\text{Hg}^{2+}] (1 + \kappa_1 X + \kappa_2 X^2 + \kappa_3 X^3 + \kappa_4 X^4) = \\ &= [\text{Hg}^{2+}] (1 + \sum \kappa_n X^n) \end{aligned} \quad (7)$$

$$[\text{Hg}^{2+}] [\text{Hg}^{\text{II}}]_{\text{total}}^{-1} = (1 + \sum \kappa_n X^n)^{-1} \quad (8_0)$$

$$[\text{HgX}^+] [\text{Hg}^{\text{II}}]_{\text{total}}^{-1} = \kappa_1 X (1 + \sum \kappa_n X^n)^{-1} \quad (8_1)$$

$$[\text{HgX}_2] [\text{Hg}^{\text{II}}]_{\text{total}}^{-1} = \kappa_2 X^2 (1 + \sum \kappa_n X^n)^{-1} \quad (8_2)$$

$$[\text{HgX}_3^-] [\text{Hg}^{\text{II}}]_{\text{total}}^{-1} = \kappa_3 X^3 (1 + \sum \kappa_n X^n)^{-1} \quad (8_3)$$

$$[\text{HgX}_4^{2-}] [\text{Hg}^{\text{II}}]_{\text{total}}^{-1} = \kappa_4 X^4 (1 + \sum \kappa_n X^n)^{-1} \quad (8_4)$$

All the ratios in (8_{0-4}) are seen to be functions of the single variable X , and independent of $[\text{Hg}^{\text{II}}]_{\text{total}}$.

Fig. 1. shows certain general trends. In each of the complex systems there is a large range of $\log X$ where almost only HgX_2 is present. This shows that the first and second halogen ions are added much more easily than the third and fourth — probably by a different type of bond. The same prevalence of the second complex was noticed for Hg^{2+} — NH_3 by J. Bjerrum⁹. For the Cd^{2+} complexes with halogen ions and other ligands, the second complex has no dominant position (Leden¹⁰). On the contrary, the existence range of CdI_2 is unusually narrow.

It is also evident from Fig. 1 that the stability of all complexes increases as we go from Cl^- to I^- .

Of all the domains in Fig. 1, those for HgX_3^- are the most uncertain since the values for $\log \kappa_3$ are less accurate than any of the other $\log \kappa_n$. However, the increase in the breadth of the HgX_3^- area from Cl^- to I^- seems to be as real as the broadening of the HgX^+ area from Cl^- to I^- .

TYPES OF BONDS

There is abundant evidence from structure investigations of vapours^{11, 12} and crystals¹³⁻¹⁶ that the molecules HgX_2 are linear or almost linear X—Hg—X ; according to Pauling¹⁷ the bonds are of sp type. It is sometimes assumed that the higher complexes are tetrahedral with sp^3 bonds²⁷. Tetrahedral bonds around a Hg are certainly present in red HgI_2 , which is built up¹⁸⁻²⁰ of sheets with coordination Hg—4I, I—2 Hg . The crystal structure of Ag_2HgI_4 (Cu_2HgI_4) can be interpreted as built up of Ag^+ (Cu^+) and tetrahedral HgI_4^{2-}

ions, although there may be some electron sharing between Ag (Cu) and I atoms, too²¹ *. On the other hand, the crystal structures of NH_4HgCl_3 and $\text{K}_2\text{HgCl}_4\text{H}_2\text{O}^{23}$ seem to be built up of HgCl_2 molecules, Cl^- ions, (H_2O molecules), and NH_4^+ (K^+) ions. In these structures every Hg is surrounded by six chlorine atoms: apart from the two firmly bound Cl, there are four Cl^- at larger distances around the «equator» of the HgCl_2 molecule. The evidence from Raman spectra does not seem to be conclusive as to whether tetrahedral HgX_4^{2-} ions exist or not²⁴⁻²⁶. As pointed out by Wells²⁷ the early structure determination²⁸ for CsHgCl_3 and CsHgBr_3 ought to be checked.

Thus it does not seem quite decided whether the HgX_4^{2-} ions in solution can be tetrahedral or always consist of linear HgX_2 molecules with loosely attached X^- ions. That higher complexes such as HgX_5^{3-} have not been observed in our experiments, whereas around the equator of HgX_2 there should be room for three or four X^- , may argue in favour of the tetrahedral bonds.

It would be desirable to study the crystal structures of a number of complex halogeno-mercurates to see whether tetrahedral HgCl_4^{2-} and HgBr_4^{2-} ions can be found or not.

MERCURY FLUORIDES

All available evidence indicates that if Hg^{2+} and F^- form complexes at all, they are much weaker than the complexes of Hg^{2+} with Cl^- , Br^- , and I^- . No solid fluo-mercurates seem to be known. Whereas all the other mercury halides have crystal structures with linear HgX_2 molecules (HgCl_2 ¹³, HgBr_2 ^{14, 15}, yellow HgI_2 ¹⁶), or with tetrahedral bonds $\text{Hg}-4 \text{I}$ (red HgI_2 ¹⁸⁻²⁰), HgF_2 has the CaF_2 structure with coordination $\text{Hg}-8 \text{F}$, which is typical of ionic compounds²⁹. From the compound $\text{HgF}_2(\text{H}_2\text{O})_2$ the water cannot be removed without decomposition and formation of HF ^{See e. g. 30}, which also indicates a bond type different from that in the other mercury(II)halides. In aqueous solutions, HgF_2 is strongly hydrolysed, the only solid hydrolysis product observed being HgO ³¹. This is easily understood if Hg^{2+} and F^- are present as free ions, since Hg^{2+} is an acid which is even slightly stronger than HF ³².

LOGARITHMIC DIAGRAMS. REDOX EMFS

Figs. 2—4 give another mode of representation, which may be advantageous for some purposes. They show how the equilibrium concentrations of the various complexes (given on a logarithmic scale) vary with X , the concentration of free X^- , in solutions where the total concentration of bivalent mercury, $[\text{Hg}^{II}]_{\text{total}}$, is kept constant at 10 mC. With increasing X the complexes

* See note, p. 552.

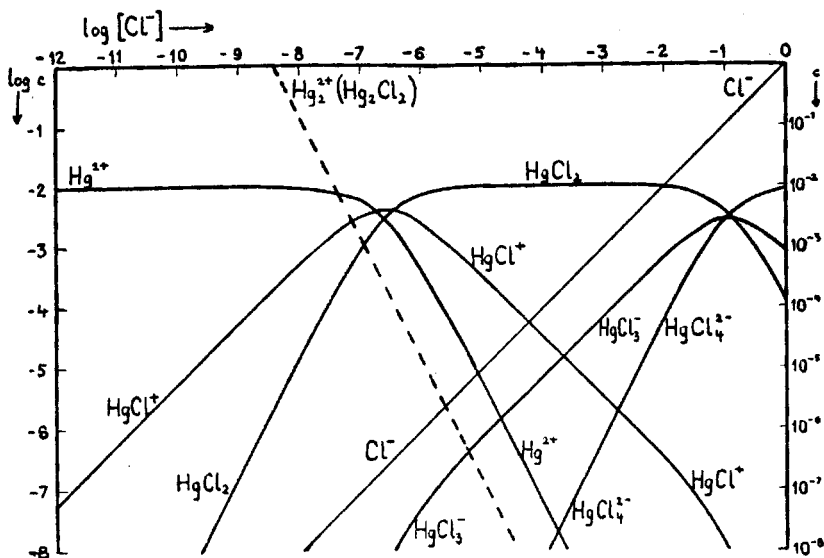
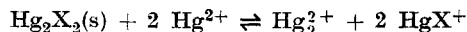


Fig. 2. Logarithmic diagram for $[Hg^{II}]_{total} = 10 \text{ mC}$ and varying $[Cl^-]$ showing the concentrations of the different $Hg^{2+} - Cl^-$ complexes. Broken line = concentration of Hg_2^{2+} in equilibrium with solid Hg_2Cl_2 .

HgX^+ , HgX_2 , and HgX_3^- are seen to increase, attain their maximum concentration and then vanish till finally HgX_4^{2-} predominates. If another $[Hg^{II}]_{total}$ is chosen, the whole set of curves will move upwards or downwards without changing their relative positions.

There are in these figures also broken lines « $Hg_2^{2+} (Hg_2X_2)$ », representing the concentration of Hg_2^{2+} in equilibrium with solid Hg_2X_2 . Thus for varying X , sets of concentrations of Hg_2^{2+} , Hg^{2+} , and HgX^+ , corresponding to the equilibrium



can be read off from the diagrams.

If a solution containing Hg_2^{2+} and Hg^{2+} is titrated with X^- , and the redox emf measured between a Pt electrode in the solution and a standard electrode, E will be given by

$$E = E_{20} + 29.58 \log q \quad (9 = I,5)$$

where E_{20} is a constant, and the quantity q is defined by

$$\log q = 2 \log [Hg^{2+}] - \log [Hg_2^{2+}] \quad (10)$$

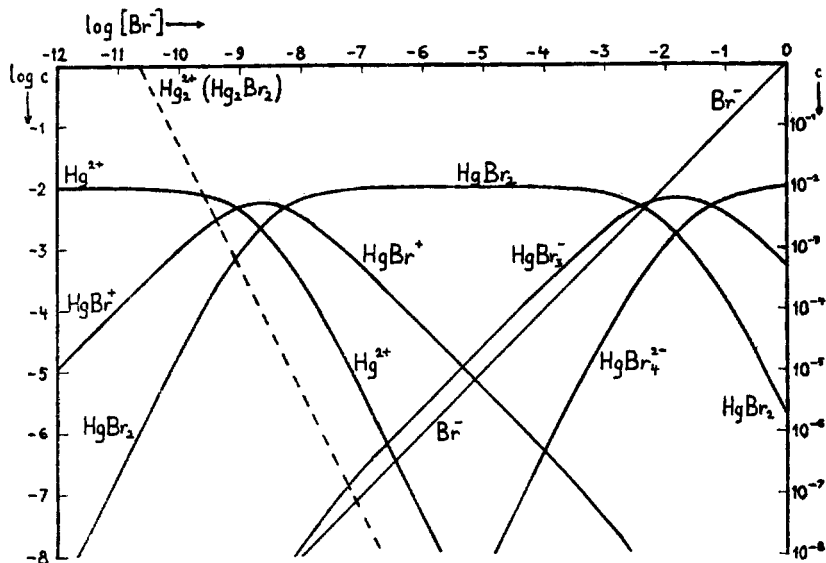


Fig. 3. Logarithmic diagram for $[Hg^{II}]_{\text{total}} = 10 \text{ mC}$ and varying $[Br^-]$ showing the concentrations of the different $Hg^{2+}-Br^-$ complexes. Broken line = concentration of Hg_2^{2+} in equilibrium with solid Hg_2Br_2 .

It can be proved from the definitions of k_s and α_1 that in the presence of solid Hg_2X_2

$$\log q = 2 \log [HgX^+] - \log k_s - 2 \log \alpha_1 \quad (11)$$

Thus $\log q$ will follow the course of $\log [HgX^+]$ in Figs. 2—4, first rise with increasing X , attain a maximum, and then decrease again (Parts IV—VI).

In the range of $\log X$ where HgX_2 predominates, the solution has a very low buffer value for X^- ions, as measured by the small increase in the quantity X_e (excess of halogen):

$$X_e = [X^-] + 2 [HgX_4^{2-}] + [HgX_3^-] - [HgX^+] - 2 [Hg^{2+}] - 2 [Hg_2^{2+}] \quad (12, \text{ cf. IV, 1, 8, 20})$$

needed for effecting a large increase in $\log X$. Thus during a titration, the solution will hurry across this range for a very small addition of X^- , and a sharp fall will occur in the curve E (or $\log q$) versus volume of X^- solution added (Part IV, Fig. 1).

At high X , the course of such a redox titration will be broken because Hg metal is precipitated by dismutation of Hg_2^{2+} ; the precipitation of Hg metal

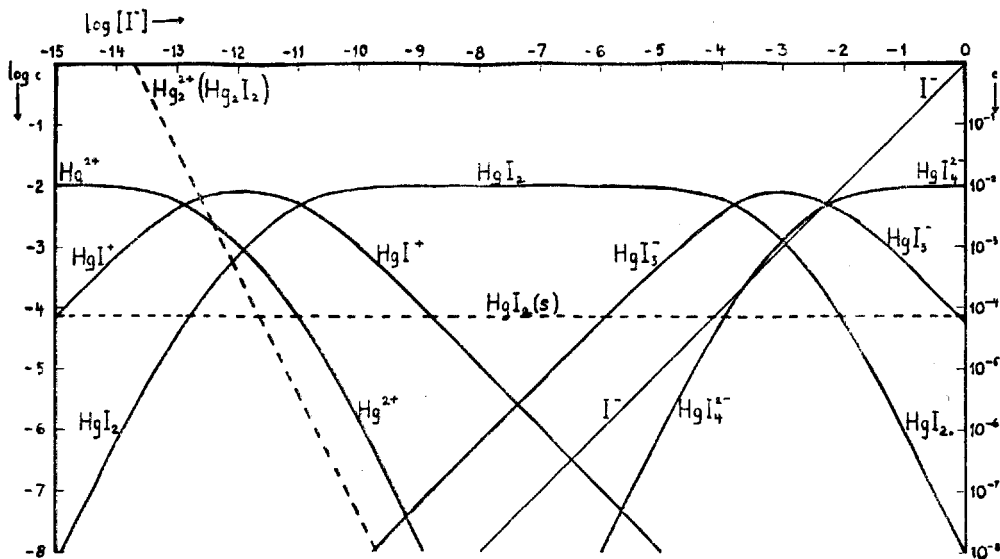


Fig. 4. Logarithmic diagram for $[Hg^{II}]_{total} = 10$ mC and varying $[I^-]$ showing the concentrations of the various $Hg^{2+}-I^-$ complexes. Broken line = concentration of Hg_2^{2+} in equilibrium with solid Hg_2I_2 . Horizontal dotted line = solubility of HgI_2 .

occurs at higher X for high $[Hg^{II}]_{total}$. The resulting equilibria are dealt with in the next section.

For I, the whole system of Hg^{II} curves is rendered meaningless in the range $[I^-] = 10^{-12.8} - 10^{-2}$ C by the precipitation of solid HgI_2 , since the concentration of HgI_2 in the solution would exceed the solubility $s = 10^{-4.13}$ C (line ' $HgI_2(s)$ '). This line does not move if $[Hg^{II}]_{total}$ is changed; at low $[Hg^{II}]_{total}$, the whole system of complex curves can thus be realized.

EQUILIBRIA WITH Hg_2X_2 AND Hg

If a solution is in equilibrium with Hg metal and with solid Hg_2X_2 , the concentrations of the different complexes of Hg^{II} are given by the formulae

$$\begin{aligned}
 [Hg^{2+}] &= k_s k_0^{-1} X^{-2} \\
 [HgX^+] &= \alpha_1 k_s k_0^{-1} X^{-1} \\
 [HgX_2] &= \alpha_2 k_s k_0^{-1} \\
 [HgX_3^-] &= \alpha_3 k_s k_0^{-1} X \\
 [HgX_4^{2-}] &= \alpha_4 k_s k_0^{-1} X^2
 \end{aligned} \tag{13}$$

as can easily be shown from the definitions of the various equilibrium constants.

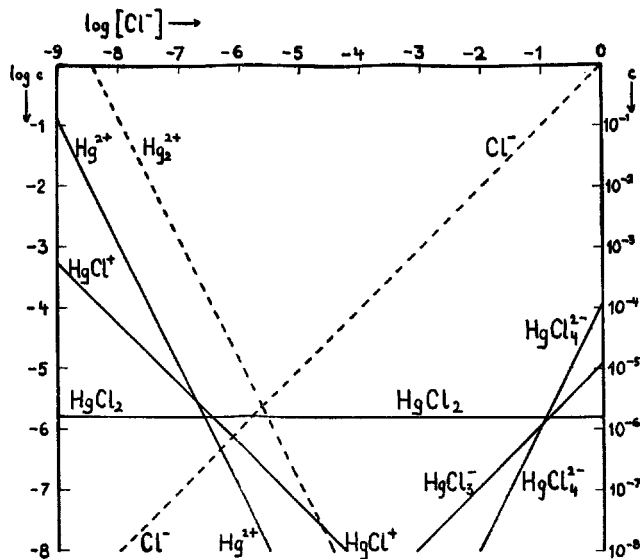
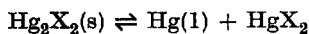


Fig. 5. Concentrations of different ionic (molecular) species in equilibrium with Hg metal and solid Hg_2Cl_2 for varying $[\text{Cl}^-]$.

In Figs. 5—7 these equilibrium concentrations (as well as $[\text{Hg}_2^{2+}] = k_s X^{-2}$) have been plotted on a logarithmic scale as functions of X for Cl^- , Br^- , and I^- .

For very low X , Hg^{II} is present chiefly as Hg^{2+} . This part of the diagram is valid for solutions of high $[\text{Hg}_2^{2+}]$. With increasing X , the total concentration of Hg^{II} decreases till it reaches a minimum value, namely the concentration of HgX_2 corresponding to the equilibrium



This concentration happens to be about the same for all three halogens.

$$\begin{aligned} [\text{HgCl}_2] &= 1.7_0 \cdot 10^{-6} \text{ C} & \log [\text{HgCl}_2] &= -5.77 \pm .03 \\ [\text{HgBr}_2] &= 0.8_5 \cdot 10^{-6} \text{ C} & \log [\text{HgBr}_2] &= -6.07 \pm .06 \\ [\text{HgI}_2] &= 1.7_4 \cdot 10^{-6} \text{ C} & \log [\text{HgI}_2] &= -5.76 \pm .04 \end{aligned} \quad (14)$$

The values in (14) have been made consistent with the two digit approximation in (4), and sometimes differ by one unit in the last figure from those given in Parts V—VII.

At still higher X , HgX_3^- and HgX_4^{2-} are formed in appreciable amounts by the reactions



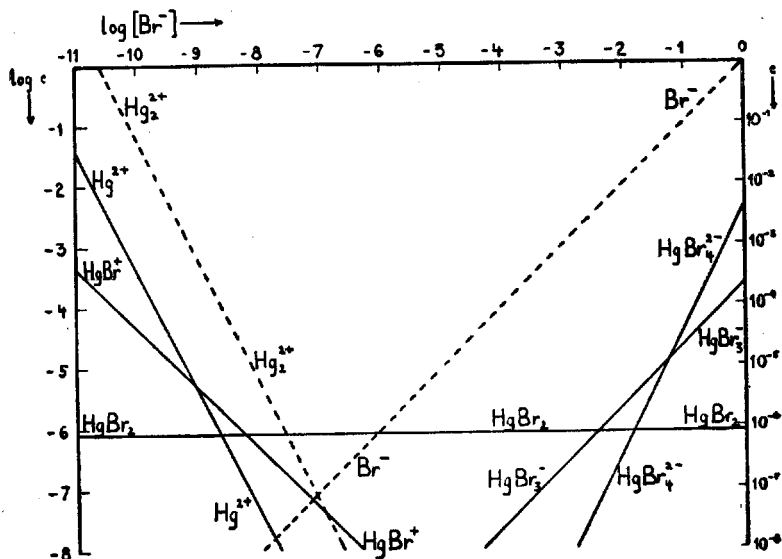


Fig. 6. Concentrations of different ionic (molecular) species in equilibrium with Hg metal and solid Hg_2Br_2 for varying $[\text{Br}^-]$.

The equilibrium amounts are highest for I. For instance with $[\text{I}^-] = 10^{-2}$ (10 mC), $[\text{HgI}_3^-] = 0.10$ mC and $[\text{HgI}_4^{2-}] = 0.18$ mC.

A given solution, containing Hg^{II} and X^- , can behave in three different ways with regard to the equilibria with Hg and Hg_2X_2 , *e. g.* (15). a) It can be in equilibrium with Hg and Hg_2X_2 simultaneously. In this case its composition is determined by X and the diagrams, Figs. 5—7. b) It can attack Hg metal with the formation of Hg_2X_2 , if $[\text{Hg}^{\text{II}}]_{\text{total}}$ is higher than that corresponding to the X of the solution and the equilibrium diagrams. In this case the solution does not attack Hg_2X_2 . c) If $[\text{Hg}^{\text{II}}]_{\text{total}}$ is lower than that corresponding to equilibrium with Hg + Hg_2X_2 , the solution will attack Hg_2X_2 with the formation of Hg metal and of more Hg^{II} . Such a solution will, on the other hand, not attack Hg metal.

From Figs. 5—7 it can be seen which of these cases applies to a given solution. For instance, a solution with $[\text{I}^-] = 10^{-1}$ would be in equilibrium with Hg and Hg_2I_2 with $[\text{Hg}^{\text{II}}]_{\text{total}} = 10^{-1.75} + 10^{-3.0} \approx 0.019$ C (Fig. 7). For lower values of $[\text{Hg}^{\text{II}}]_{\text{total}}$, the reaction $\text{Hg}_2\text{I}_2 + 2 \text{I}^- \rightleftharpoons \text{HgI}_4^{2-} + \text{Hg}(1)$ will proceed to the right (Hg_2I_2 attacked but not Hg), for higher $[\text{Hg}^{\text{II}}]_{\text{total}}$ it goes to the left (Hg attacked but not Hg_2I_2).

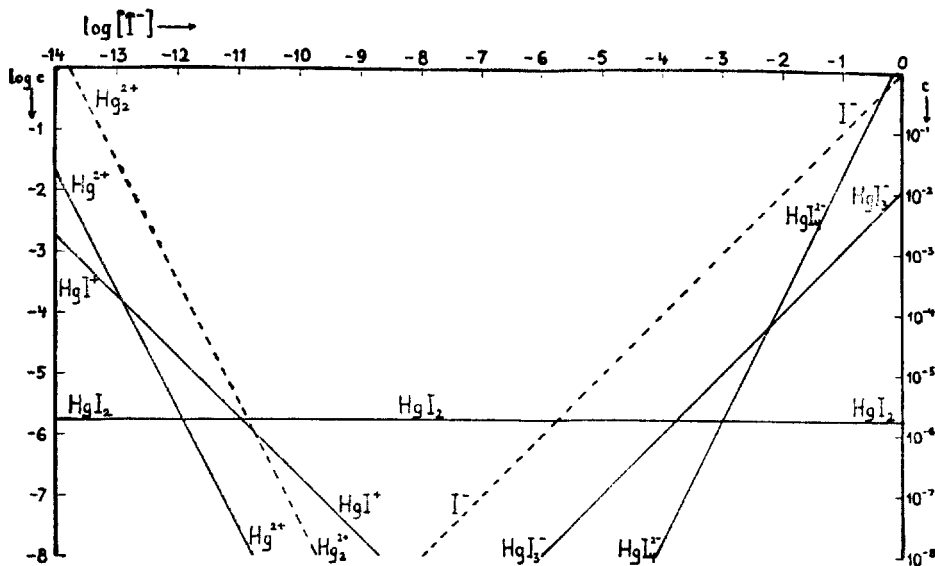


Fig. 7. Concentration of different ionic (molecular) species in equilibrium with Hg metal and solid Hg_2I_2 for varying $[I^-]$.

EQUILIBRIA WITH SOLID HgI_2

In Fig. 8 are shown in a logarithmic scale the concentrations of the complexes in equilibrium with solid (red) HgI_2 :

$$\begin{aligned}
 [Hg^{2+}] &= s\kappa_2^{-1}X^{-2} \\
 [HgI^+] &= \kappa_1 s \kappa_2 X^{-1} \\
 [HgI_2] &= s \\
 [HgI_3^-] &= \kappa_3 s \kappa_2^{-1} X \\
 [HgI_4^{2-}] &= \kappa_4 s \kappa_2^{-1} X^2
 \end{aligned} \tag{16}$$

These formulae can also easily be deduced from the definitions of the various equilibrium constants. Actually the lines in Fig. 8 are identical with those in Fig. 7 only that they are all (except, of course, the I^- curve) displaced upwards by $1.63 = \log sk_0 k_s^{-1} \kappa_2^{-1}$, since the solubility s of red HgI_2 is $10^{1.63} = 43$ times larger than the concentration $\kappa_2 k_s k_0^{-1}$ of HgI_2 in equilibrium with Hg_2I_2 and Hg.

Of course the equilibrium described in any one of the diagrams in this paper becomes fictitious when the concentration of one of the ions becomes so large that the ionic strength, 0.5 C, is exceeded.

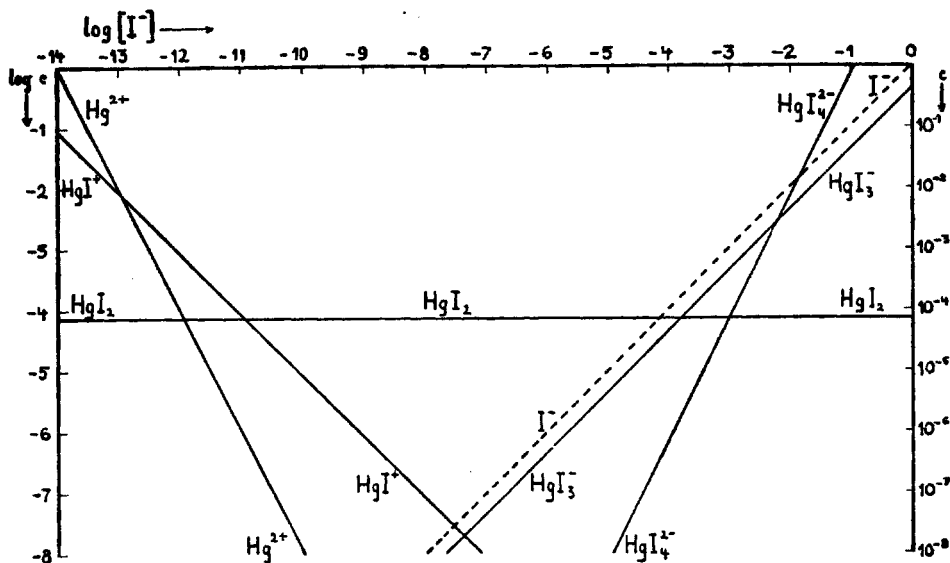


Fig. 8. Concentrations of Hg^{2+} and its complexes with I^- in equilibrium with solid HgI_2 for varying $[\text{I}^-]$.

ON THE THERMODYNAMIC CONSTANTS

All the equilibrium constants given are valid under the special conditions of our experiments: 25°C , $[\text{H}^+] = 10\text{ mC}$, and ionic strength = 500 mC (by addition of NaClO_4). Now that it seems certain that we need only count with the ionic species mentioned in (1), one might repeat the measurements for lower ionic strengths in order to find the thermodynamic constants. However, an extrapolation to ionic strength zero must be rendered difficult by the fact that Hg^{2+} is an acid of considerable strength so that the concentration of H^+ must not be too low if its hydrolysis is to be held back. Then the ionic strength will at any rate be at least about 10 mC , so that the assignment of activity factors to the various ionic species cannot be very accurate.

At the ionic strength chosen for our experiments, no general formulae for the activity factors hold good, since the individual properties of the ions cannot be neglected. For our ionic medium, the products of the ionic activity factors for Hg_2Cl_2 , Hg_2Br_2 , and Hg_2I_2 seem to be about 0.09 — 0.13 ^{7,p.517}, and the activity factor for uncharged HgI_2 about 1.4 ⁸. If it is assumed that Hg_2^{2+} and Hg^{2+} have about the same activity factors, it can be concluded that the values for $\log \kappa_2$ and $\log \kappa_3$ for infinite dilution are about one unit higher than those found for our ionic medium; $\log \kappa_1$ and $\log \kappa_2$ should also be higher for infinite dilution, though the difference should be less.

The acidity of Hg_2^{2+} and Hg^{2+} , the standard potentials of mercury, and the value for k_0 at infinite dilution will be discussed in papers by Hietanen and Sillén³² and Forsling and Sillén³³.

SUMMARY

The complexes of Hg^{2+} with Cl^- , Br^- , and I^- have been studied at 25° C by electrometric methods using solutions with $[\text{H}^+] = 10 \text{ mC}$ and ionic strength 500 mC (by addition of NaClO_4).

Complexes of the types HgX^+ , HgX_2 , HgX_3^- , and HgX_4^{2-} were proved to exist for all three halogens, whereas there was no need for assuming the existence of other complexes.

The logarithms of the complex products $\kappa_1 \dots \dots \kappa_4$ (defined by 2) were found to be:

	$\log \kappa_1$	$\log \kappa_2$	$\log \kappa_3$	$\log \kappa_4$
for $\text{Hg}^{2+} - \text{Cl}^-$	$6.74 \pm .02$	$13.22 \pm .02$	$14.07 \pm .15$	$15.07 \pm .06$
for $\text{Hg}^{2+} - \text{Br}^-$	$9.05 \pm .03$	$17.33 \pm .04$	$19.74 \pm .11$	$21.00 \pm .03$
for $\text{Hg}^{2+} - \text{I}^-$	$12.87 \pm .03$	$23.82 \pm .04$	$27.60 \pm .14$	$29.83 \pm .02$

The logarithms of the solubility products k_s were, under the conditions chosen,

for Hg_2Cl_2 $-16.88 \pm .01$, for Hg_2Br_2 $-21.29 \pm .04$, and
for Hg_2I_2 $-27.47 \pm .01$.

Diagrams are given showing the distribution of Hg^{II} over the different complexes for varying concentrations of free X^- , and illustrating the equilibria with Hg metal and solid Hg_2X_2 , for I also with solid HgI_2 .

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* *Note added in proof:* According to a private communication, Professor P. M. Harris and Mr. A. F. Foster (Ohio State University, Columbus; Ohio) have found extra lines in the powder photographs of low-temperature Ag_2HgI_4 , indicating that the real unit cell contains eight formula units. The crystal structure previously given²¹ is thus subject to revision.

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ERRATA IN PREVIOUS PARTS

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|-----------------------------------|--|
| Part II: p. 64, line 4 from below | for '5.8 ± 0.5' read '5.8 ± 0.3' |
| Part III: p. 467, head of Table 3 | for '½ X _c ' read '-½ X _c ' |
| p. 470, formula (21) | for 'X = (X ⁻) + etc.' read 'X _c =
= (X ⁻) + etc.' |
| Part V: p. 487, line 5 from below | for (0.227 ± 0.26) read (0.227 ± 0.026) |