

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

LARS GUNNAR SILLÉN

*Institute of Inorganic and Physical Chemistry, University, Stockholm, Sweden, and Institute of Inorganic Chemistry, Chalmers' Institute of Technology, Gothenburg, Sweden*

In the seven preceding publications<sup>1-7</sup> the work of a team investigating the equilibria between  $\text{Hg}^{2+}$  and the halogen ions  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  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  $\text{Hg}^{2+}$ — $\text{HgX}^+$ — $\text{HgX}_2$  have as far as we know not been investigated since 1908. On the equilibria involving  $\text{HgX}_2$ — $\text{HgX}_3^-$ — $\text{HgX}_4^{2-}$  somewhat more work has been done. However, the investigators of the latter equilibria can be divided into two groups. Some have assumed that only  $\text{HgX}_3^-$  appears in appreciable amounts, and neglected  $\text{HgX}_4^{2-}$ . The others have, on the contrary, neglected  $\text{HgX}_3^-$  and assumed that only  $\text{HgX}_4^{2-}$  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  $\text{Hg}^{2+}$ -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  $\text{NaClO}_4$  as salt medium. In this way the activity factors were kept approximately constant; otherwise the calculations would have been hopelessly complicated.

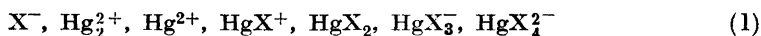
At high concentrations  $[\text{Br}^-]$  and  $[\text{I}^-]$  it was possible to measure the concentration of free  $\text{Hg}^{2+}$ , using a Hg electrode (Parts VI and VII). In no other

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  $\text{Hg}_2^{2+}$  and  $\text{Hg}^{2+}$ , generally in equilibrium with solid  $\text{Hg}_2\text{X}_2$ . For interpreting these emfs it was necessary also to know the solubility products of the mercury(I)halides,  $\text{Hg}_2\text{X}_2$ , 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  $\text{I}^-$  is only preliminary). Part III deals with measurements of the solubility products for the  $\text{Hg}_2\text{X}_2$ , 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  $\text{X}^-$  are added to a  $\text{Hg}_2^{2+} - \text{Hg}^{2+}$  mixture. The equilibria are rather complicated, since solid  $\text{Hg}_2\text{X}_2$  appears in addition to the various  $\text{Hg}^{2+} - \text{X}^-$  complexes. Finally, parts V—VII deal with the measurements for the individual halogens,  $\text{Cl}^-$  (part V),  $\text{Br}^-$  (part VI), and  $\text{I}^-$  (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  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ .

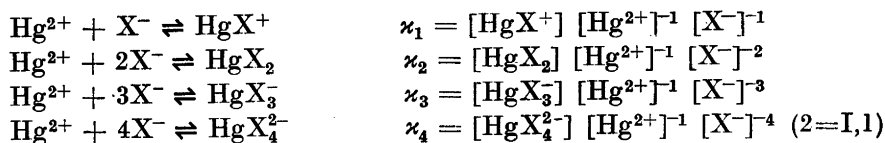
#### EQUILIBRIUM CONSTANTS

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

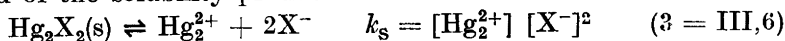


It was not possible to neglect the existence of any one of the  $\text{Hg}^{2+} - \text{X}^-$  complexes. On the other hand there was no need to assume that, for instance, univalent mercury also forms single ions  $\text{Hg}^+$  or soluble complexes  $\text{Hg}_2\text{X}^+$ , or that there are higher complexes of bivalent mercury such as  $\text{HgX}_5^{2-}$  and  $\text{HgX}_6^{4-}$  or polynuclear complexes such as  $\text{Hg}_2\text{X}_5^-$ ,  $\text{Hg}_3\text{X}_8^{2-}$ , 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  $\text{Hg}^{\text{II}}$  complexes may appear at higher total  $\text{Hg}^{\text{II}}$  concentrations than those used by us, which were generally  $\leq 10$  mC.

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



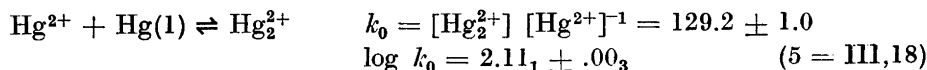
and of the solubility products



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

	X = Cl	Br	I	
log $\kappa_1$	6.74 ± .02	9.05 ± .03	12.87 ± .03	
log $\kappa_2$	13.22 ± .02	17.33 ± .04	23.82 ± .04	
log $\kappa_3$	14.07 ± .15	19.74 ± .11	27.60 ± .14	
log $\kappa_4$	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  $\text{HgI}_2$  according to Biedermann and Sillén<sup>8</sup>:

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

these constants permit the calculation for each halogen of all equilibria involving the above mentioned molecular species (1) in solution, Hg metal, and solid  $\text{Hg}_2\text{X}_2$  (for I also solid  $\text{HgI}_2$ ).

#### 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,  $\text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$ . The ordinate goes from 0 to 100 and shows the percentage of the total amount of  $\text{Hg}^{\text{II}}$  present in the form of different com-

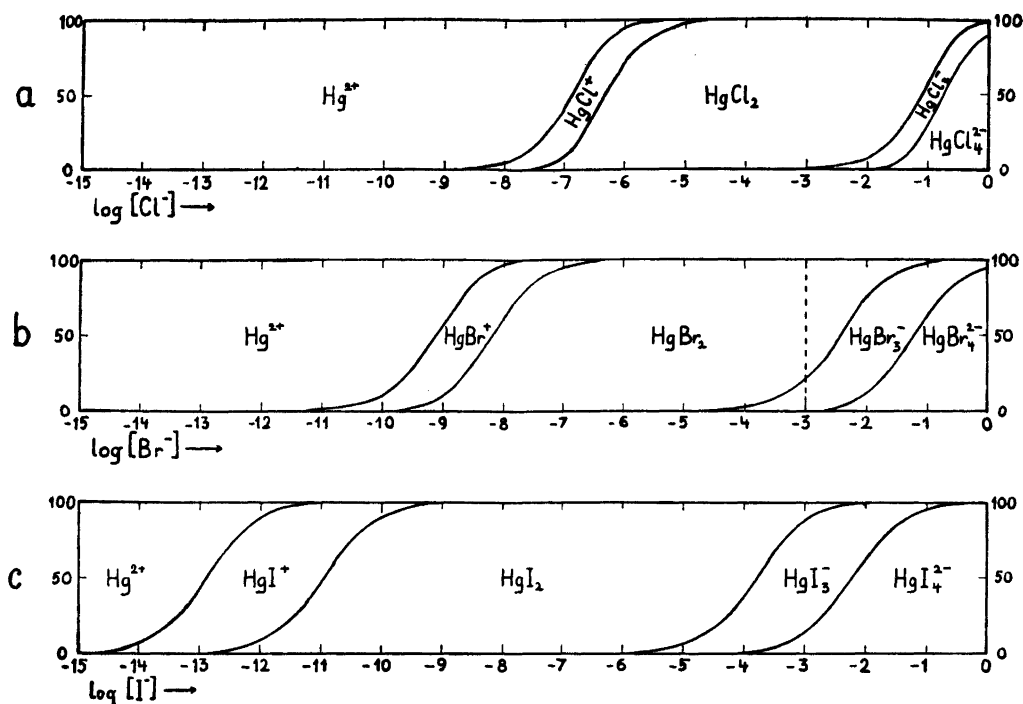


Fig. 1. Distribution of  $\text{Hg}^{\text{II}}$  over different complexes with a)  $\text{Cl}^-$  b)  $\text{Br}^-$  c)  $\text{I}^-$  for varying  $[\text{X}^-]$ . The abscissa is  $\log [\text{X}^-]$ . On the ordinate axis the distance 0—100 represents the total amount of  $\text{Hg}^{\text{II}}$  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.  $\text{HgX}_3$ , represents the fraction of the total amount of  $\text{Hg}^{\text{II}}$  present as that complex.

plexes at the  $[\text{X}^-]$  given. For example, we see that in a bromide solution containing 1 mC free  $\text{Br}^-$  ( $\log [\text{Br}^-] = -3$ , dotted line in Fig. 1b) about 20 % of all  $\text{Hg}^{\text{II}}$  is present as  $\text{HgBr}_3^-$ , and about 80 % as  $\text{HgBr}_2$ ; other complexes are negligible. With 10 mC free  $\text{Br}^-$  ( $\log [\text{Br}^-] = -2$ ), about 12 % of all  $\text{Hg}^{\text{II}}$  is present as  $\text{HgBr}_4^{2-}$ , about 63 % as  $\text{HgBr}_3^-$ , and about 25 % as  $\text{HgBr}_2$ . At higher  $[\text{Br}^-]$ ,  $\text{HgBr}_4^{2-}$  becomes the predominant complex. Between  $[\text{Br}^-] = 10^{-4}$  and  $10^{-7}$ , there is a broad range with  $\text{HgBr}_2$  dominating. At lower  $[\text{Br}^-]$ , the amounts of  $\text{HgBr}^+$  and  $\text{Hg}^{2+}$  become considerable. At  $[\text{Br}^-] = 10^{-9}$ , we have, for instance, 9 %  $\text{HgBr}_2$ , 48 %  $\text{HgBr}^+$ , and 43 %  $\text{Hg}^{2+}$ . Below  $[\text{Br}^-] = 10^{-11}$  C practically only  $\text{Hg}^{2+}$  is present.

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

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

$$\begin{aligned} [\text{HgX}^+] &= \kappa_1 [\text{Hg}^{2+}]X; & [\text{HgX}_2] &= \kappa_2 [\text{Hg}^{2+}]X^2 \\ [\text{HgX}_3^-] &= \kappa_3 [\text{Hg}^{2+}]X^3; & [\text{HgX}_4^{2-}] &= \kappa_4 [\text{Hg}^{2+}]X^4 \end{aligned}$$

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

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

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

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

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

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

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  $\text{HgX}_2$  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  $\text{Hg}^{2+}$ — $\text{NH}_3$  by J. Bjerrum<sup>9</sup>. For the  $\text{Cd}^{2+}$  complexes with halogen ions and other ligands, the second complex has no dominant position (Leden<sup>10</sup>). On the contrary, the existence range of  $\text{CdI}_2$  is unusually narrow.

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

Of all the domains in Fig. 1, those for  $\text{HgX}_3^-$  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  $\text{HgX}_3^-$  area from  $\text{Cl}^-$  to  $\text{I}^-$  seems to be as real as the broadening of the  $\text{HgX}^+$  area from  $\text{Cl}^-$  to  $\text{I}^-$ .

#### TYPES OF BONDS

There is abundant evidence from structure investigations of vapours<sup>11, 12</sup> and crystals<sup>13-16</sup> that the molecules  $\text{HgX}_2$  are linear or almost linear  $\text{X—Hg—X}$ ; according to Pauling<sup>17</sup> the bonds are of  $sp$  type. It is sometimes assumed that the higher complexes are tetrahedral with  $sp^3$  bonds<sup>27</sup>. Tetrahedral bonds around a Hg are certainly present in red  $\text{HgI}_2$ , which is built up<sup>18-20</sup> of sheets with coordination  $\text{Hg—4I, I—2 Hg}$ . The crystal structure of  $\text{Ag}_2\text{HgI}_4$  ( $\text{Cu}_2\text{HgI}_4$ ) can be interpreted as built up of  $\text{Ag}^+$  ( $\text{Cu}^+$ ) and tetrahedral  $\text{HgI}_4^{2-}$

ions, although there may be some electron sharing between Ag (Cu) and I atoms, too<sup>21</sup> \*. On the other hand, the crystal structures of  $\text{NH}_4\text{HgCl}_3$  and  $\text{K}_2\text{HgCl}_4\cdot\text{H}_2\text{O}$ <sup>23</sup> seem to be built up of  $\text{HgCl}_2$  molecules,  $\text{Cl}^-$  ions, ( $\text{H}_2\text{O}$  molecules), and  $\text{NH}_4^+$  ( $\text{K}^+$ ) ions. In these structures every Hg is surrounded by six chlorine atoms: apart from the two firmly bound Cl, there are four  $\text{Cl}^-$  at larger distances around the «equator» of the  $\text{HgCl}_2$  molecule. The evidence from Raman spectra does not seem to be conclusive as to whether tetrahedral  $\text{HgX}_4^{2-}$  ions exist or not<sup>24-26</sup>. As pointed out by Wells<sup>27</sup> the early structure determination<sup>28</sup> for  $\text{CsHgCl}_3$  and  $\text{CsHgBr}_3$  ought to be checked.

Thus it does not seem quite decided whether the  $\text{HgX}_4^{2-}$  ions in solution can be tetrahedral or always consist of linear  $\text{HgX}_2$  molecules with loosely attached  $\text{X}^-$  ions. That higher complexes such as  $\text{HgX}_5^{3-}$  have not been observed in our experiments, whereas around the equator of  $\text{HgX}_2$  there should be room for three or four  $\text{X}^-$ , 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  $\text{HgCl}_4^{2-}$  and  $\text{HgBr}_4^{2-}$  ions can be found or not.

#### MERCURY FLUORIDES

All available evidence indicates that if  $\text{Hg}^{2+}$  and  $\text{F}^-$  form complexes at all, they are much weaker than the complexes of  $\text{Hg}^{2+}$  with  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ . No solid fluo-mercurates seem to be known. Whereas all the other mercury halides have crystal structures with linear  $\text{HgX}_2$  molecules ( $\text{HgCl}_2$ <sup>13</sup>,  $\text{HgBr}_2$ <sup>14, 15</sup>, yellow  $\text{HgI}_2$ <sup>16</sup>), or with tetrahedral bonds  $\text{Hg}-4 \text{I}$  (red  $\text{HgI}_2$ <sup>18-20</sup>),  $\text{HgF}_2$  has the  $\text{CaF}_2$  structure with coordination  $\text{Hg}-8 \text{F}$ , which is typical of ionic compounds<sup>29</sup>. From the compound  $\text{HgF}_2(\text{H}_2\text{O})_2$  the water cannot be removed without decomposition and formation of  $\text{HF}$ <sup>See e. g. 30</sup>, which also indicates a bond type different from that in the other mercury(II)halides. In aqueous solutions,  $\text{HgF}_2$  is strongly hydrolysed, the only solid hydrolysis product observed being  $\text{HgO}$ <sup>31</sup>. This is easily understood if  $\text{Hg}^{2+}$  and  $\text{F}^-$  are present as free ions, since  $\text{Hg}^{2+}$  is an acid which is even slightly stronger than  $\text{HF}$ <sup>32</sup>.

#### 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*  $\text{X}^-$ , in solutions where the total concentration of bivalent mercury,  $[\text{Hg}^{\text{II}}]_{\text{total}}$ , is kept constant at 10 mC. With increasing  $X$  the complexes

\* See note, p. 552.

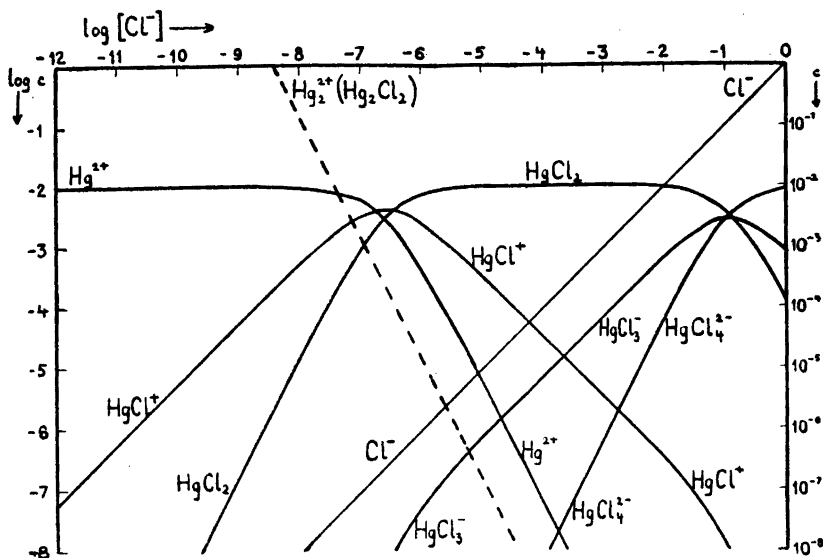
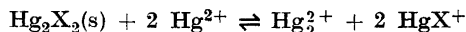


Fig. 2. Logarithmic diagram for  $[Hg^{II}]_{total} = 10 \text{ mC}$  and varying  $[Cl^-]$  showing the concentrations of the different  $Hg^{2+}-Cl^-$  complexes. Broken line = concentration of  $Hg_2^{2+}$  in equilibrium with solid  $Hg_2Cl_2$ .

$HgX^+$ ,  $HgX_2$ , 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

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

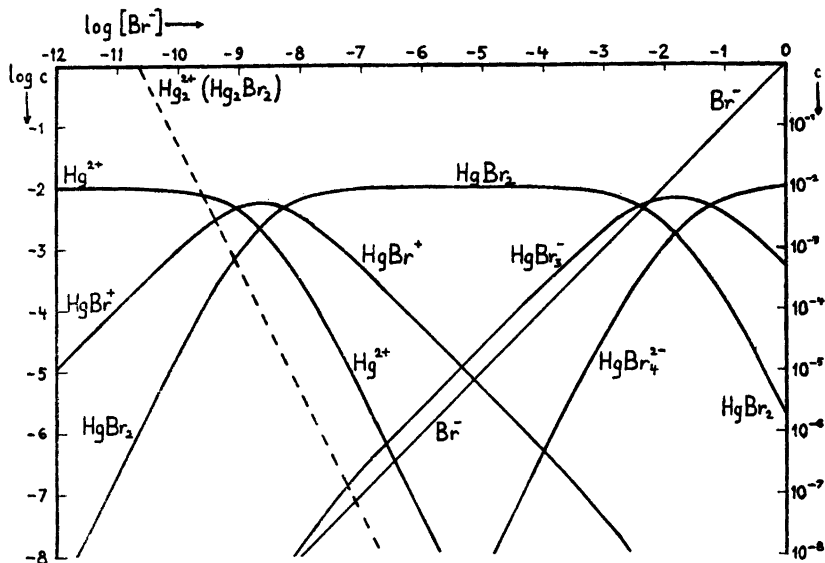


Fig. 3. Logarithmic diagram for  $[Hg^{II}]_{total} = 10$  mC and varying  $[Br^-]$  showing the concentrations of the different  $Hg^{2+}-Br^-$  complexes. Broken line = concentration of  $Hg_2^{2+}$  in equilibrium with solid  $Hg_2Br_2$ .

It can be proved from the definitions of  $k_s$  and  $\alpha_1$  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



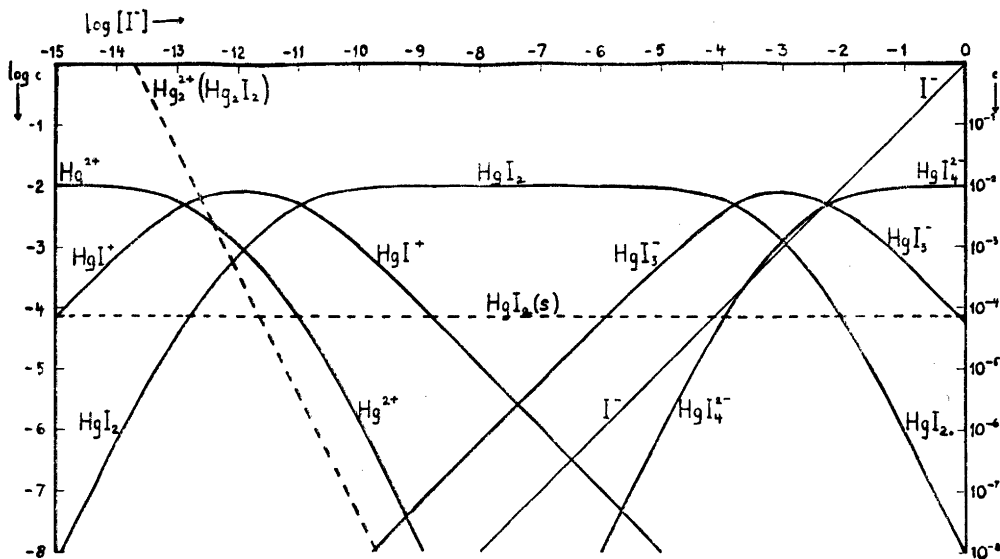


Fig. 4. Logarithmic diagram for  $[\text{Hg}^{\text{II}}]_{\text{total}} = 10 \text{ mC}$  and varying  $[\text{I}^-]$  showing the concentrations of the various  $\text{Hg}^{2+} - \text{I}^-$  complexes. Broken line = concentration of  $\text{Hg}_2^{2+}$  in equilibrium with solid  $\text{Hg}_2\text{I}_2$ . Horizontal dotted line = solubility of  $\text{HgI}_2$ .

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

For I, the whole system of  $\text{Hg}^{\text{II}}$  curves is rendered meaningless in the range  $[\text{I}^-] = 10^{-12.8} - 10^{-2} \text{ C}$  by the precipitation of solid  $\text{HgI}_2$ , since the concentration of  $\text{HgI}_2$  in the solution would exceed the solubility  $s = 10^{-4.13} \text{ C}$  (line ' $\text{HgI}_2(\text{s})$ '). This line does not move if  $[\text{Hg}^{\text{II}}]_{\text{total}}$  is changed; at low  $[\text{Hg}^{\text{II}}]_{\text{total}}$ , the whole system of complex curves can thus be realized.

#### EQUILIBRIA WITH $\text{Hg}_2\text{X}_2$ AND Hg

If a solution is in equilibrium with Hg metal and with solid  $\text{Hg}_2\text{X}_2$ , the concentrations of the different complexes of  $\text{Hg}^{\text{II}}$  are given by the formulae

$$\begin{aligned}
 [\text{Hg}^{2+}] &= k_s k_0^{-1} X^{-2} \\
 [\text{HgX}^+] &= \alpha_1 k_s k_0^{-1} X^{-1} \\
 [\text{HgX}_2] &= \alpha_2 k_s k_0^{-1} \\
 [\text{HgX}_3^-] &= \alpha_3 k_s k_0^{-1} X \\
 [\text{HgX}_4^{2-}] &= \alpha_4 k_s k_0^{-1} X^2
 \end{aligned} \tag{13}$$

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

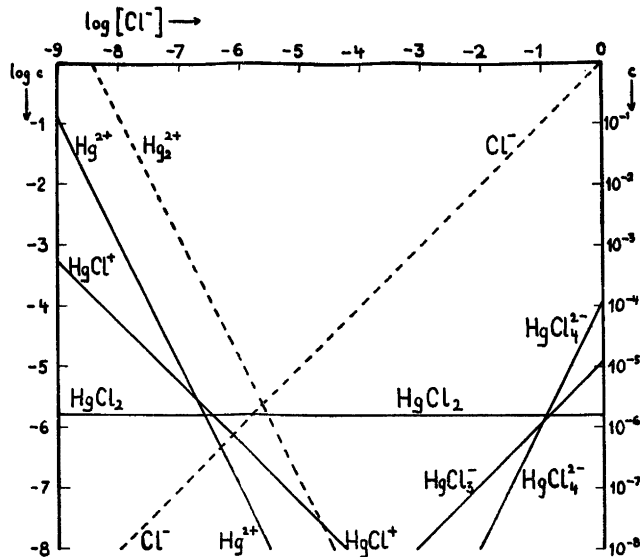
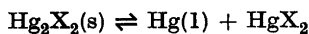


Fig. 5. Concentrations of different ionic (molecular) species in equilibrium with Hg metal and solid  $\text{Hg}_2\text{Cl}_2$  for varying  $[\text{Cl}^-]$ .

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  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ .

For very low  $X$ ,  $\text{Hg}^{\text{II}}$  is present chiefly as  $\text{Hg}^{2+}$ . This part of the diagram is valid for solutions of high  $[\text{Hg}_2^{2+}]$ . With increasing  $X$ , the total concentration of  $\text{Hg}^{\text{II}}$  decreases till it reaches a minimum value, namely the concentration of  $\text{HgX}_2$  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  $X$ ,  $\text{HgX}_3^-$  and  $\text{HgX}_4^{2-}$  are formed in appreciable amounts by the reactions



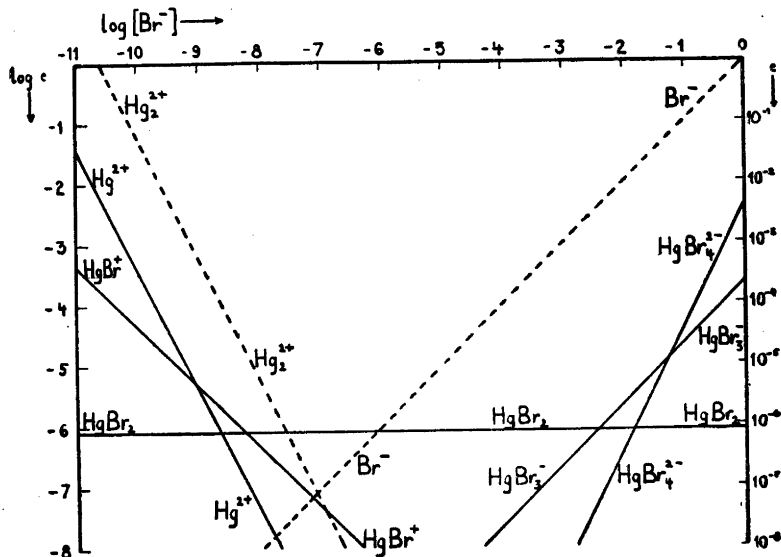


Fig. 6. Concentrations of different ionic (molecular) species in equilibrium with Hg metal and solid  $\text{Hg}_2\text{Br}_2$  for varying  $[\text{Br}^-]$ .

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  $\text{Hg}^{\text{II}}$  and  $\text{X}^-$ , can behave in three different ways with regard to the equilibria with Hg and  $\text{Hg}_2\text{X}_2$ , *e. g.* (15). a) It can be in equilibrium with Hg and  $\text{Hg}_2\text{X}_2$  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  $\text{Hg}_2\text{X}_2$ , 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  $\text{Hg}_2\text{X}_2$ . c) If  $[\text{Hg}^{\text{II}}]_{\text{total}}$  is lower than that corresponding to equilibrium with Hg +  $\text{Hg}_2\text{X}_2$ , the solution will attack  $\text{Hg}_2\text{X}_2$  with the formation of Hg metal and of more  $\text{Hg}^{\text{II}}$ . 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  $\text{Hg}_2\text{I}_2$  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 ( $\text{Hg}_2\text{I}_2$  attacked but not Hg), for higher  $[\text{Hg}^{\text{II}}]_{\text{total}}$  it goes to the left (Hg attacked but not  $\text{Hg}_2\text{I}_2$ ).

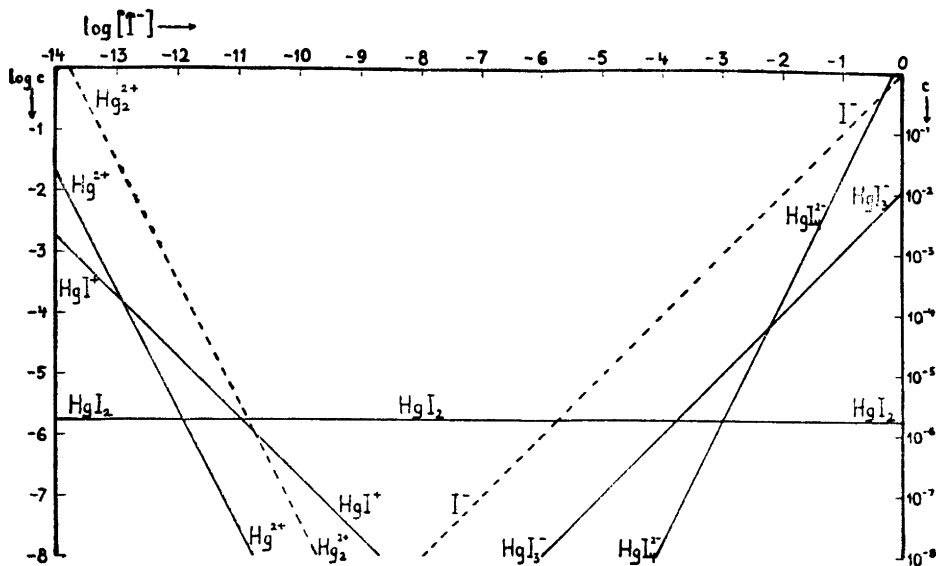


Fig. 7. Concentration of different ionic (molecular) species in equilibrium with Hg metal and solid  $\text{Hg}_2\text{I}_2$  for varying  $[\text{I}^-]$ .

#### EQUILIBRIA WITH SOLID $\text{HgI}_2$

In Fig. 8 are shown in a logarithmic scale the concentrations of the complexes in equilibrium with solid (red)  $\text{HgI}_2$ :

$$\begin{aligned}
 [\text{Hg}^{2+}] &= s\kappa_2^{-1}X^{-2} \\
 [\text{HgI}^+] &= \kappa_1 s\kappa_2 X^{-1} \\
 [\text{HgI}_2] &= s \\
 [\text{HgI}_3^-] &= \kappa_3 s\kappa_2^{-1}X \\
 [\text{HgI}_4^{2-}] &= \kappa_4 s\kappa_2^{-1}X^2
 \end{aligned} \tag{16}$$

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  $\text{I}^-$  curve) displaced upwards by  $1.63 = \log sk_0k_s^{-1}\kappa_2^{-1}$ , since the solubility  $s$  of red  $\text{HgI}_2$  is  $10^{1.63} = 43$  times larger than the concentration  $\kappa_2 k_s k_0^{-1}$  of  $\text{HgI}_2$  in equilibrium with  $\text{Hg}_2\text{I}_2$  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.

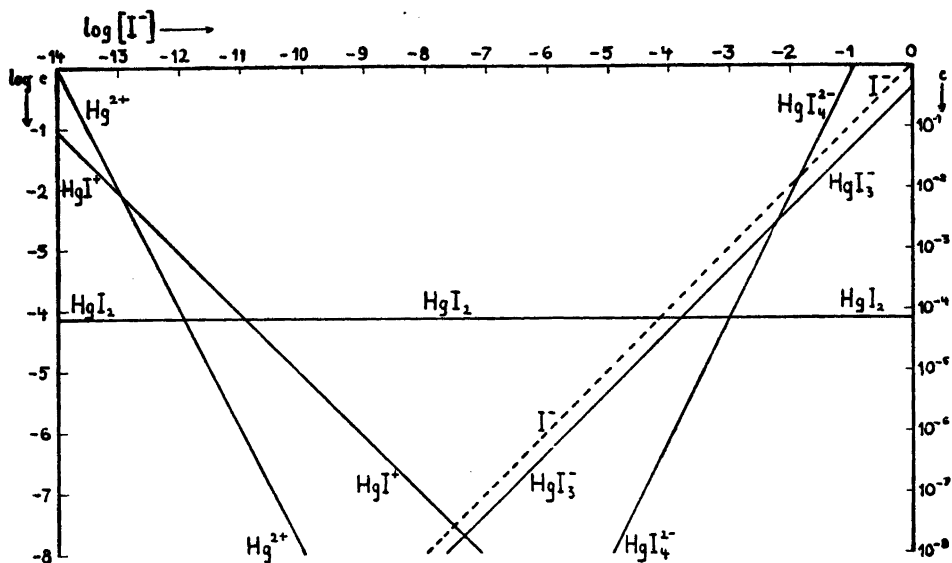


Fig. 8. Concentrations of  $\text{Hg}^{2+}$  and its complexes with  $\text{I}^-$  in equilibrium with solid  $\text{HgI}_2$  for varying  $[\text{I}^-]$ .

#### ON THE THERMODYNAMIC CONSTANTS

All the equilibrium constants given are valid under the special conditions of our experiments:  $25^\circ\text{C}$ ,  $[\text{H}^+] = 10\text{ mC}$ , and ionic strength =  $500\text{ mC}$  (by addition of  $\text{NaClO}_4$ ). 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  $\text{Hg}^{2+}$  is an acid of considerable strength so that the concentration of  $\text{H}^+$  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  $10\text{ mC}$ , 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  $\text{Hg}_2\text{Cl}_2$ ,  $\text{Hg}_2\text{Br}_2$ , and  $\text{Hg}_2\text{I}_2$  seem to be about  $0.09$ — $0.13$ <sup>7,p.517</sup>, and the activity factor for uncharged  $\text{HgI}_2$  about  $1.4$ <sup>8</sup>. If it is assumed that  $\text{Hg}_2^{2+}$  and  $\text{Hg}^{2+}$  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  $\text{Hg}_2^{2+}$  and  $\text{Hg}^{2+}$ , the standard potentials of mercury, and the value for  $k_0$  at infinite dilution will be discussed in papers by Hietanen and Sillén<sup>32</sup> and Forsling and Sillén<sup>33</sup>.

#### SUMMARY

The complexes of  $\text{Hg}^{2+}$  with  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  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  $\text{NaClO}_4$ ).

Complexes of the types  $\text{HgX}^+$ ,  $\text{HgX}_2$ ,  $\text{HgX}_3^-$ , and  $\text{HgX}_4^{2-}$  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  $\text{Hg}_2\text{Cl}_2$   $-16.88 \pm .01$ , for  $\text{Hg}_2\text{Br}_2$   $-21.29 \pm .04$ , and  
for  $\text{Hg}_2\text{I}_2$   $-27.47 \pm .01$ .

Diagrams are given showing the distribution of  $\text{Hg}^{\text{II}}$  over the different complexes for varying concentrations of free  $\text{X}^-$ , and illustrating the equilibria with Hg metal and solid  $\text{Hg}_2\text{X}_2$ , for I also with solid  $\text{HgI}_2$ .

Finally, I wish once more to express my gratitude for the favour of cooperating with Mr Per Olof Bethge, Mr Gunnar Infeldt (fil.kand.), Mrs Inga Jonevall-Westöo, Mr Arne Jonsson, Mr Bengt Lindgren (fil.lic.), and Miss Ingegerd Qvarfort.

Mrs Inger Brattsten (fil.lic., leg.apot.), Mr Erik Ekedahl, Miss Sirkka Hietanen (fil.mag.), Mr Herbert Larsson, Mr Bengt Liljeqvist (fil.kand.) and Mr Sven Sahlqvist have given valuable aid in many respects, as has been gratefully acknowledged in previous papers. I should also like to thank Miss Karin Ehrnström and Miss Aina Norström for their helpful assistance in the preparation of the present paper.

\* *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  $\text{Ag}_2\text{HgI}_4$ , indicating that the real unit cell contains eight formula units. The crystal structure previously given<sup>21</sup> is thus subject to revision.

## REFERENCES

1. Sillén, L. G. *Svensk Kem. Tid.* **58** (1946) 52 (Part I).
2. Sillén, L. G., and Infeldt, G. *Svensk Kem. Tid.* **58** (1946) 61 (Part II).
3. Jonsson, A., Qvarfort, I, and Sillén, L. G. *Acta Chem. Scand.* **1** (1947) 461 (Part III).
4. Sillén, L. G. *Acta Chem. Scand.* **1** (1947) 473 (Part IV).
5. Lindgren, B., Jonsson, A., and Sillén, L. G. *Acta Chem. Scand.* **1** (1947) 479 (Part V).
6. Bethge, P. O., Jonevall-Westöö, I., and Sillén, L. G. *Acta Chem. Scand.* **2** (1948) 828 (Part VI).
7. Qvarfort, I, and Sillén, L. G. *Acta Chem. Scand.* **3** (1949) (Part VII).
8. Biedermann, G., and Sillén, L. G. *Svensk Kem. Tid.* **61** (1949) 63.
9. Bjerrum, J. Diss. Copenhagen (1941) p. 287.
10. Leden, I. Diss. Lund (1943) p. 114.
11. Braune, H., and Knoke, S. *Z. physik. Chem.* **B 23** (1933) 163.
12. Gregg, A. H., Hampson, G. C., Jenkins, G. I., Jones, P. L. F., and Sutton, L. E. *Trans. Faraday Soc.* **33** (1937) 852.
13. Braekken, H., and Scholten, W. *Z. Krist.* **89** (1934) 448.
14. Verweel, H. J., and Bijvoet, J. M. *Z. Krist.* **77** (1931) 122.
15. Braekken, H., *Z. Krist.* **81** (1932) 152.
16. Gorsky, W. S. *Phys. Z. Sowjetunion* **5** (1934) 367.
17. Pauling, L. *The nature of the chemical bond.* 2nd ed. (1940) p. 89.
18. Claassen, A. Diss. Amsterdam (1926).
19. Bijvoet, J. M., Claassen, A., and Karssen, A. *Proc. Acad. Sci. Amsterdam* **29** (1926) 529.
20. Huggins, M. L., and Magill, P. L. *J. Am. Chem. Soc.* **49** (1927) 2357.
21. Ketelaar, J. A. A. *Z. Krist.* **80** (1931) 190.
22. Harmsen, E. J. *Z. Krist.* **100** (1938) 208.
23. Mac Gillavry, C. H., de Wilde, J. H., and Bijvoet, J. M. *Z. Krist.* **100** (1938) 212.
24. Bernstein, H. J., and Martin, W. H. *Trans. Roy. Soc. Can.* **III 31** (1937) 95.
25. Nayar, M. R., and Saraf, J. R. *J. Indian Chem. Soc.* **20** (1943) 312.
26. Kohlrausch, K. W. F. *Ramanspektren (Hand- u. Jahrb. d. Chem. Physik* **9 VI**) Leipzig (1943) 418–419.
27. Wells, A. F. *Structural inorganic chemistry.* Oxford (1945) 513–515.
28. Natta, G., and Passerini, L. *Gazz. chim. ital.* **58** (1928) 472.
29. Ebert, F., and Woitinek, H. *Z. anorg. allg. Chem.* **210** (1933) 269.
30. Ruff, O., and Bahlau, G. *Ber.* **51** (1918) 1752.
31. Jaeger, A. *Z. anorg. Chem.* **27** (1901) 25.
32. Hietanen, S., and Sillén, L. G. To be published.
33. Forsling, W., and Sillén, L. G. To be published.

Received May 27, 1949.

## ERRATA IN PREVIOUS PARTS

- |                                   |  |
|-----------------------------------|--|
| 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 <sub>c</sub> ' read '-½ X <sub>c</sub> '  |
| p. 470, formula (21)              | for 'X = (X <sup>-</sup> ) + etc.' read 'X <sub>c</sub> =<br>= (X <sup>-</sup> ) + etc.' |
| Part V: p. 487, line 5 from below | for (0.227 ± 0.26) read (0.227 ± 0.026)  |