

Electrometric Investigation of Equilibria between Mercury and Halogen Ions

IV. Redox Titrations of Hg(I,II) Solutions with Halogen Ions

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If a solution S containing Hg^{2+} , Hg_2^{2+} , and an excess of solid Hg_2X_2 is titrated with a solution T of a halogen ion $\text{X}^- = \text{Cl}^-$ or Br^- , and the redox emf is plotted against the volume of T added, a curve is obtained similar to those in Fig. 1. (For I^- , the curve is complicated by precipitation of HgI_2). E first rises slowly to a maximum and then falls off rather rapidly. The curve is steepest in the neighbourhood of the point where almost all mercury is present either as HgX_2 or as Hg_2X_2 ($X_e = 0$, see below), and then gradually flattens out. Incidentally, similar titration curves were obtained by Müller and Aarflot¹, who concluded that it is impossible to determine Hg^{2+} and Hg_2^{2+} separately by titration with halogen.

It will now be demonstrated that such titrations, together with the data collected in Parts I—III^{2, 3, 4} of this series, will give sufficient information

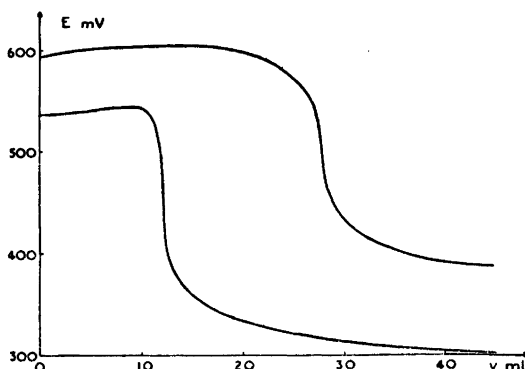


Fig. 1. Redox titrations with excess of Hg_2Cl_2 . Upper curve: S = 10 mC Hg^{2+} , 1 mC Hg_2^{2+} , T = 10 mC Hg^{2+} , 100 mC Cl^- . Lower curve: S = 0.93 mC Hg^{2+} , 2.0 mC Hg_2^{2+} , T = 0.93 mC Hg^{2+} , 50 mC Cl^- .

for calculating the complex products κ_1 , κ_2 , κ_3 , and κ_4 for Hg^{2+} and the halogen ion in question. To be specific, κ_1 and κ_2 can be calculated from the maximum value of E , whereas κ_3 and κ_4 are obtained from the lower part of the curve.

In our experiments, we always tried to use the same total concentration a of Hg^{II} in S and T. For the calculations it is convenient to introduce the quantity X_e , the concentration of halogen in excess over that needed for forming HgX_2 and Hg_2X_2 (cf. III,9):

$$X_e = (X_{\text{total}}) - 2(\text{Hg}^{\text{II}})_{\text{total}} - 2(\text{Hg}_2^{2+})_{\text{total}} \quad (1)$$

In the first part of the curve, X_e is negative. It increases during the titration and passes through zero at the steepest point. In the latter part it is then positive.

If we intended to study the first part of the curve, X_e in S was of course negative. If, on the other hand, only the latter part of the curve was to be studied, it was also possible to begin with a positive X_e in S.

THE MAXIMUM VALUE OF E .

The emf of the cell can be written according to (I, 5) or (III, 3)

$$E = E_{20} + 29.58 \log[(\text{Hg}^{2+})^2 (\text{Hg}_2^{2+})^{-1}] \quad (2)$$

As solid Hg_2X_2 is present, according to (III,6) and (I,1)

$$(\text{Hg}^{2+})^2 (\text{Hg}_2^{2+})^{-1} = (\text{Hg}^{2+})^2 (\text{X}^-)^2 k_s^{-1} = (\text{HgX}^+)^2 \kappa_1^{-2} k_s^{-1} \quad (3)$$

By (2), (3), and (III,6)

$$E = E_{20} + E_{10} - E_{1X} + 59.16 \log[(\text{HgX}^+) \kappa_1^{-1}] \quad (4)$$

Thus E is a function of (HgX^+) only, which might have been expected from the fact that the electrode reaction can be written $2 \text{HgX}^+ + 2e^- = \text{Hg}_2\text{X}_2$ (s)

If the total concentration of Hg^{II} remains constant = a , it was shown in (II,6) that the maximum value of $(\text{HgX}^+) = \alpha_1 a$ is reached when $(\text{Hg}^{2+}) = (\text{HgX}_2)$ and

$$(\text{HgX}^+)_{\text{max}} = a \sqrt{k_{12}} (2 + \sqrt{k_{12}})^{-1} = a \kappa_1 \kappa_2^{-\frac{1}{2}} (2 + \sqrt{k_{12}})^{-1} \quad (5)$$

(See II,1.) At this point E will also have a maximum. By inserting (5) into (4) we find

$$E_{\max} - 59.16 \log a = E_{20} + E_{10} - E_{1X} - 59.16 \log (2 + \sqrt{k_{12}}) - 29.58 \log \kappa_2 \quad (6)$$

If our assumptions are correct, $(E_{\max} - 59.16 \log a)$ should thus remain constant when a is varied. As all quantities in the right hand side of (6) except κ_2 are known from previous measurements, we can obtain κ_2 from E_{\max} and a , and thus by means of (II,1) also κ_1 .

E AS A FUNCTION OF X_e (FOR NEGATIVE X_e)

We shall now derive a relation between the two experimental quantities: E which is measured directly and X_e which can easily be calculated if we know the composition of the solutions S and T and the volume v of T added to 100 ml of S.

In the first part of the titration, where X_e is negative, the only soluble molecules that need be considered are Hg^{2+} , HgX^+ , HgX_2 and Hg_2^{2+} :

$$\begin{aligned} (\text{Hg}_2^{2+})_{\text{total}} &= (\text{Hg}_2^{2+}) + (\text{Hg}_2\text{X}_2)_{\text{solid}} \\ (\text{Hg}^{2+})_{\text{total}} &= (\text{Hg}^{2+}) + (\text{HgX}^+) + (\text{HgX}_2) = a \\ (\text{X}^-)_{\text{total}} &= 2(\text{Hg}_2\text{X}_2)_{\text{solid}} + (\text{HgX}^+) + 2(\text{HgX}_2) \end{aligned} \quad (7)$$

With (1) we find

$$-X_e = 2(\text{Hg}_2^{2+}) + 2(\text{Hg}^{2+}) + (\text{HgX}^+) \quad (8)$$

We introduce the parameter

$$z = X \sqrt{\kappa_2} = (\text{HgX}_2)^{\frac{1}{2}} (\text{Hg}^{2+})^{-\frac{1}{2}} \quad (9)$$

and remember that $k_{12} = \kappa_1^2 \kappa_2^{-1}$ according to (II,1)

This and the equilibrium conditions gives:

$$(\text{HgX}^+) = (\text{Hg}^{2+}) \kappa_1 X = (\text{Hg}^{2+}) z \sqrt{k_{12}} \quad (10a)$$

$$(\text{HgX}_2) = (\text{Hg}^{2+}) \kappa_2 X^2 = (\text{Hg}^{2+}) z^2 \quad (10b)$$

$$(\text{Hg}_2^{2+}) = k_s X^{-2} = k_s \kappa_2 z^{-2} \quad (11)$$

By (7) and (10) we find

$$\begin{aligned} (\text{Hg}^{2+}) &= a(1 + z \sqrt{k_{12}} + z^2)^{-1}; (\text{HgX}^+) = az \sqrt{k_{12}} (1 + z \sqrt{k_{12}} + z^2)^{-1} \\ (\text{HgX}_2) &= az^2 (1 + z \sqrt{k_{12}} + z^2)^{-1} \end{aligned} \quad (12)$$

If (12) is introduced in (4) we find

$$\begin{aligned} E &= E_{20} + E_{10} - E_{1X} + 59.16 \log a + 59.16 \log [z (1 + z \sqrt{k_{12}} + z^2)^{-1}] \\ &- 29.58 \log \kappa_2 \end{aligned} \quad (13)$$

If (13) is combined with (6) we see that $E = E_{\max}$ for $z = 1$ and that

$$E_{\max} - E = 59.16 \log[(z^{-1} + \sqrt{k_{12}} + z) (2 + \sqrt{k_{12}})^{-1}] \quad (14)$$

The relation between X_e and z is found from (11), (12) and (8):

$$-X_e = 2k_1 \kappa_2 z^{-2} + a(2z^{-1} + \sqrt{k_{12}}) (z^{-1} + \sqrt{k_{12}} + z)^{-1} \quad (15)$$

Thus if k_{12} , k_1 , and κ_2 are known, E and X_e can be calculated by means of (14) and (15) for round values of the parameter z , plotted and compared with a plot of the experimental values.

THE CALCULATION OF q_1 AND q_2 .

For the discussion of the lower part of the titration curve we shall transform our expression (2) for E . By means of (I,1) we find

$$E = E_{2X} + 59.16 \log (\text{HgX}_2) - 59.16 \log X \quad (16)$$

$$\text{where } E_{2X} = E_{20} + E_{10} - E_{1X} - 59.16 \log \kappa_2 \quad (17)$$

Thus E_{2X} can be calculated from quantities determined by experiments already described.

If the composition corresponds to a point in the lower part of the titration curve, only HgX_2 , HgX_3^- , HgX_4^{2-} , and X^- seem to be present in appreciable amount in the solution. From (I,2), the definition of q_1 and q_2 , we find

$$(\text{HgX}_3^-) = q_1 X (\text{HgX}_2) \quad ; \quad (\text{HgX}_4^{2-}) = q_2 X^2 (\text{HgX}_2) \quad (18)$$

Moreover

$$(\text{HgX}_2) + (\text{HgX}_3^-) + (\text{HgX}_4^{2-}) = a = (\text{HgX}_2) (1 + q_1 X + q_2 X^2) \quad (19)$$

$$X_e = (X^-) + (\text{HgX}_3^-) + 2(\text{HgX}_4^{2-}) = X[1 + (q_1 + 2q_2 X) (\text{HgX}_2)] \quad (20)$$

From (19) and (20)

$$X_e = X[1 + a(q_1 + 2q_2X) (1 + q_1X + q_2X^2)^{-1}] \quad (21)$$

and from (16) and (19)

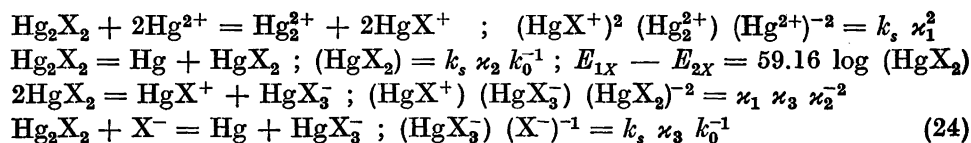
$$\begin{aligned} 59.16 \log (1 + q_1X + q_2X^2) &= E_{2X} + 59.16 \log a - E - 59.16 \log X = \\ &= 59.16 \log r \end{aligned} \quad (22)$$

These are the equations needed. Every titration gives a number of pairs (E, X_e) . First X_e is inserted instead of X in (22), which gives an approximate value r' of $r = 1 + q_1X + q_2X^2$. By plotting $(r' - 1)X_e^{-1} \approx q_1 + q_2X$ against X_e approximate values of q_1 and q_2 are obtained. By means of these and (21), X_e is calculated for round values of X , and a table of the correction $-(X_e - X)$ for different X_e is constructed. By interpolation in this table, better values of X are calculated, and inserted in (22), and the function

$$F_1 = (r - 1) X^{-1} = q_1 + q_2X \quad (23)$$

calculated and plotted against X . The values obtained in this graph will generally be accurate enough; otherwise the procedure can be repeated. The latter part of this calculation reminds one of the method introduced by Leden⁵.

From the lower part of the titration curve it is thus possible to find values of q_1 and q_2 , from which κ_3 and κ_4 can be calculated by means of (I,2). In principle it is also possible to deduce from these titration curves whether there are considerable amounts of complexes with more than 4 X^- or of complexes with more than one Hg^{2+} under the experimental conditions. By combining the equilibrium constants κ_1 , κ_2 , κ_3 , κ_4 , and k_s some other equilibria of interest can be calculated, such as for example



SUMMARY.

When a mixture of Hg^{2+} and Hg_2^{2+} is titrated with Cl^- or Br^- , the redox potential describes a curve similar to those in Fig. 1. It is demonstrated how such curves can be used for calculating the complex constants for Hg^{2+}

— X^- ; the maximum E in the upper part gives the constants κ_1 and κ_2 , and the lower part gives κ_3 and κ_4 .

REFERENCES

1. Müller, E., and Aarflot, H. *Rec. trav. chim.* **43** (1924) 874.
2. Sillén, L. G. *Svensk Kem. Tid.* **58** (1946) 52 (Part I).
3. Sillén, L. G., and Infeldt, G. *Svensk Kem. Tid.* **58** (1946) 61 (Part II).
4. Jonsson, A., Qvarfort, I., and Sillén, L. G. *Acta Chem. Scand.* **1** (1947) 461 (Part III).
5. Leden, I. Diss. Lund (1943).

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