331. *The Ultra-violet Absorption Spectra of Mercurous Perchlorate Solutions.*

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The marked ultra-violet light absorption of the dimeric mercurous ion in the wave-length range 200—300 mμ. enables concentrations of mercurous perchlorate down to 3×10^{-6}M. to be determined in dilute perchloric acid solutions by means of a spectrophotometer.

It is suggested that deviations from Beer's law, which become apparent at concentrations below 10^{-6}M-mercurous perchlorate, show a significant degree of dissociation of the dimer at these concentrations, leading to a value of $K_{\text{diss.}} = [\text{Hg}^+]^2/[\text{Hg}_2^{++}]$ within the limits 10^{-8} and 10^{-6}.

IN an attempt to find a simple method for estimating concentrations of mercurous mercury as low as 10^{-5}M., the absorption spectrum of mercurous perchlorate in dilute perchloric acid was investigated. Considerable absorption was found in the wave-length range 200—300 mμ., with absorption maxima at 209 and 236·5 mμ., corresponding to those observed for the sulphate at 214 and 240 mμ. (Kato, *Bull. Inst. Phys. Chem. Res. Japan*, 1930, **12**, 230). The molecular extinction coefficient at 236·5 mμ. (the more pronounced maximum) was found to be of the order $2·8 \times 10^4$ and was thus sufficiently large to justify further investigation of the possibilities of this method.

EXPERIMENTAL.

Reagents were of AnalaR quality unless otherwise stated. Metallic mercury was purified by drawing air through the metal for several days, followed by passage through columns of dilute nitric acid and distilled water, and finally by distillation under reduced pressure. Silver perchlorate was prepared from AnalaR materials by Hill's method (*J. Amer. Chem. Soc.*, 1921, **43**, 254).

Mercurous perchlorate solution, 0·0509M. in mercurous perchlorate and 0·0341M. in perchloric acid, was prepared and standardised against 0·0594M-sodium chloride solution by use of bromophenol-blue as adsorption indicator (Pugh, *J.*, 1937, 1824). This stock solution was kept over a few grams of metallic mercury. A more dilute stock solution, prepared by dilution of the 0·0509M-mercurous perchlorate solution with dilute perchloric acid, was standardised potentiometrically against $1·484 \times 10^{-3}$M-sodium chloride solution (Müller and Aarflot, *Rec. Trav. chim.*, 1924, **43**, 874). This solution, $5·10 \times 10^{-4}$M. in mercurous perchlorate and $1·04 \times 10^{-2}$M. in perchloric acid, was not kept in contact with metallic mercury, but nevertheless remained unaltered for 4 months as shown by subsequent titration, and also by the constant optical density at 236·5 mμ. of samples diluted ten times.

Perchloric acid solutions were standardised against standard baryta with bromothymol-blue as indicator. The perchloric acid (60%) used was shown by potentiometric titration against mercurous perchlorate to contain approximately 7×10^{-6} mole of chloride ion per mole of perchloric acid. In mercurous perchlorate solutions of concentration 3×10^{-6}M. and above, this impurity had no noticeable effect on the optical density up to a concentration of about 0·05M-perchloric acid, *i.e.*, [Cl$^-$] = $3·5 \times 10^{-7}$M. At higher perchloric acid concentrations, or at mercurous concentrations of the order of 10^{-6}M. and less, even with 10^{-2}M-perchloric acid, there was an appreciable diminution in the expected optical density when the untreated acid was used, presumably owing to the formation of calomel or a chloride complex. For measurements at these concentrations, perchloric acid of lower chloride-ion content was prepared by the addition of sufficient silver perchlorate solution to give an excess of $3·2 \times 10^{-4}$M. of silver ion in a 9M-perchloric acid solution. Vigorous shaking coagulated the silver chloride precipitate, which was removed by passing the solution through a No. 3 sintered-glass filter. The treated solutions thus contained $3·5 \times 10^{-5}$ mole of silver perchlorate per mole of perchloric acid, and the chloride ion remaining, the silver chloride solubility product in 9M-perchloric acid being assumed equal to that in water, was of the order 6×10^{-8} mole per mole of perchloric acid.

A solution of Hopkin and Williams's sodium perchlorate was treated similarly, and the resulting solutions contained $1·7 \times 10^{-4}$ mole of silver perchlorate per mole of sodium perchlorate. The proportion of chloride ion remaining was again of the order 6×10^{-8} mole per mole of sodium perchlorate. These treated perchloric acid or sodium perchlorate solutions were employed in all cases where their use, as compared with untreated solutions, was found to cause an appreciable alteration in the optical density, *i.e.*, in those instances referred to above.

The spectrophotometers used were, for 1-cm. optical length cells a Unicam model SP 500 quartz spectrophotometer, and for 5-cm. cells a Beckman model DU quartz spectrophotometer. Measurements were made at room temperature, approximately 18°.

RESULTS AND DISCUSSION.

Optical-density Measurements as a Method of determining Mercurous Perchlorate Concentrations.—The highest concentration of mercurous perchlorate for which the full molecular extinction curve between 200 and 300 mμ. can satisfactorily be determined with a cell of 1-cm.

optical length is of the order 5×10^{-5}M., and the corresponding optical density at the most pronounced absorption maximum ($\lambda = 236\cdot5$ mμ.) is approximately $1\cdot4$. At this wave-length Beer's law is apparently obeyed over the concentration range $[Hg_2(ClO_4)_2] = 5 \times 10^{-5}$—$3 \times 10^{-6}$M.; $[HClO_4] = 10^{-2}$M. (Fig. 1, curve A). Similar measurements at concentrations of perchloric acid between 10^{-3}M. and 10^{-1}M. gave, for corresponding concentrations of mercurous perchlorate, values of the optical density identical within experimental error. The addition of sodium perchlorate up to a concentration of 10^{-1}M. ($[HClO_4] = 10^{-3}$M.) also caused no observable change. The value of $\varepsilon_{obs.}$ at $236\cdot5$ mμ. under these conditions is $(2\cdot78 \pm 0\cdot02) \times 10^4$.

FIG. 1.
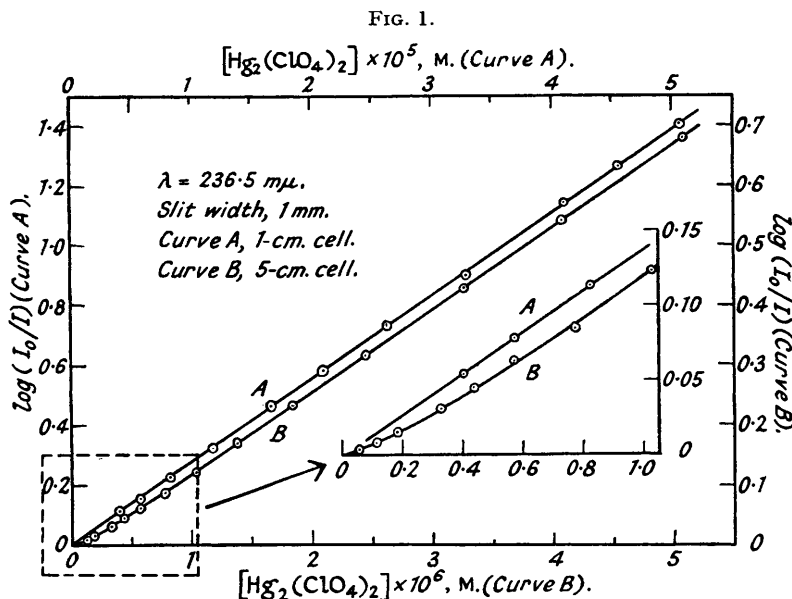
To extend the concentration range of mercurous perchlorate which can be determined, plots of $\log(I_0/I)$ against $[Hg_2(ClO_4)_2]$ (c) were constructed from measurements at longer wave-lengths. In all cases these plots were linear and passed through the origin; the results are

TABLE I.

| λ(mμ.).	$Hg_2(ClO_4)_2$, concn. range (moles per l.).	$\varepsilon_{obs.} = \log (I_0/I)/cl.$*	Slit width, mm.	$[HClO_4]$ (moles per l.).
295	$5\cdot1 \times 10^{-2}$—$2\cdot0 \times 10^{-3}$	30·4	0·5	$3\cdot4 \times 10^{-2}$
275	$5\cdot6 \times 10^{-3}$—$1\cdot6 \times 10^{-4}$	254	0·5	$3\cdot4 \times 10^{-2}$
260	$4\cdot4 \times 10^{-4}$—$2\cdot0 \times 10^{-5}$	3480	1·0	$3\cdot4 \times 10^{-2}$
254	$1\cdot6 \times 10^{-4}$—$7\cdot3 \times 10^{-6}$	8500	1·0	$3\cdot4 \times 10^{-2}$
236·5	$5\cdot1 \times 10^{-5}$—$3\cdot0 \times 10^{-6}$	$(2\cdot78 \pm 0\cdot02) \times 10^4$	1·0	10^{-3}—10^{-1}

* Optical length of cell, 1 cm.

summarised in Table I. The values of $\varepsilon_{obs.}$ except at $236\cdot5$ mμ. are probably not accurately reproducible from one instrument to another, as in this part of the spectrum the molecular extinction increases rapidly with decreasing wave-length, and the wave-length calibration of a spectrophotometer may differ from the true value by as much as $0\cdot5$ mμ. in this region. Nevertheless, for a given wave-length setting and slit width of a particular instrument, the use of longer wave-lengths than $236\cdot5$ mμ. enables the range of concentrations which can be determined to be increased up to 5×10^{-2}M.-mercurous perchlorate, provided that the concentration can be found in one instance by another method.

The Effect of Acid Strength and Salt Concentration on $\varepsilon_{obs.}$.—At concentrations of perchloric acid smaller than 10^{-3}M., the value of $\varepsilon_{obs.}$ at $236\cdot5$ mμ. was found to be less than $2\cdot78 \times 10^4$, the effect increasing with decreasing acidity. This was not investigated in detail but is probably due to the formation of a hydroxyl complex.

Above concentrations of 10^{-1}M. of added perchloric acid or sodium perchlorate there is a small effect of salt concentration on the molecular extinction curve. Fig. 2 shows plots of $(\varepsilon_{obs.})_\lambda$ against λ for various concentrations of perchloric acid and sodium perchlorate. In addition to a decrease in the value of $\varepsilon_{obs.}$ for the main absorption peak, there is also a small shift of the whole extinction curve to the ultra-violet, most pronounced at the shorter wavelengths. At the main maximum, the decrease in $\varepsilon_{obs.}$ is linear with concentration and $(\varepsilon_{obs.})_{max.}$ is given for perchloric acid by $(\varepsilon_{obs.})_{max.} = (2 \cdot 78 - 0 \cdot 055[\text{HClO}_4]) \times 10^4$, and for sodium perchlorate by $(\varepsilon_{obs.})_{max.} = (2 \cdot 78 - 0 \cdot 035[\text{NaClO}_4]) \times 10^4$, the concentrations being expressed in moles per litre. The corresponding movement of the wave-length is also linear in concentration, and the position of the absorption maximum varies from $236 \cdot 5$ mμ. in 10^{-3}—10^{-1}M- to $233 \cdot 5$ mμ. in $8 \cdot 08$M-perchloric acid. In the presence of $4 \cdot 38$M-sodium perchlorate, the wave-length of maximum absorption is $235 \cdot 5$ mμ. These relationships were obtained from measurements at nine different concentrations of perchloric acid over the range $0 \cdot 1$—$8 \cdot 08$M.,

FIG. 2.
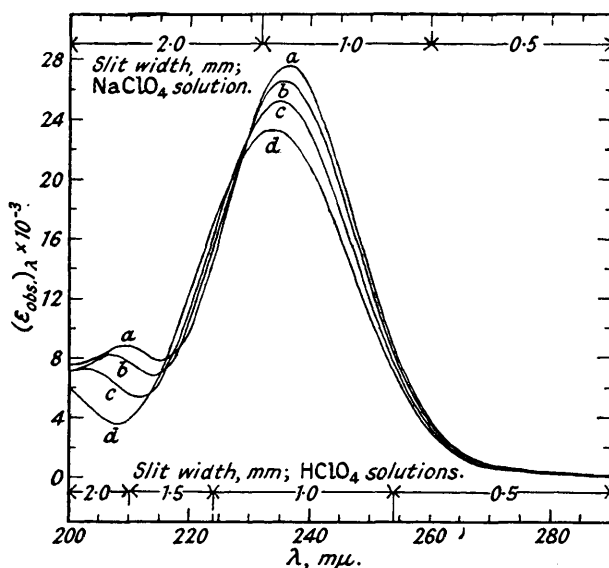
(a) $0 \cdot 05$M-HClO$_4$.
(b) $\begin{cases} 1 \cdot 80\text{M-HClO}_4 \text{ and} \\ 2 \cdot 90\text{M-NaClO}_4, \ 1 \cdot 04 \times 10^{-3}\text{M-HClO}_4. \end{cases}$
(c) $4 \cdot 49$M-HClO$_4$.
(d) $8 \cdot 08$M-HClO$_4$.

[Hg$_2$(ClO$_4$)$_2$] $= 5 \cdot 07 \times 10^{-5}$M. (1-cm. cell).

and at six different concentrations of sodium perchlorate over the range zero to $4 \cdot 38$M. In the latter measurements the perchloric acid concentration was maintained constant at $1 \cdot 04 \times 10^{-3}$M.

As the concentrations of acid or salt added are large, these relatively small effects may be due merely to a change in the physical nature of the solvent medium rather than to chemical association. It thus seems that the light absorption is due to mercurous mercury, and that in the range 10^{-3}—10^{-1}M-perchloric acid at least, the formation of hydroxyl ion or perchlorate ion complexes is negligible. This was partly confirmed by measurements on mercurous nitrate in $1 \cdot 04 \times 10^{-3}$M-nitric acid which gave a value of $(\varepsilon_{obs.})_{236 \cdot 5}$ of $2 \cdot 79 \times 10^4$, and the extinction curve from 300 mμ. to 230 mμ. was similar to that obtained with mercurous perchlorate in $1 \cdot 04 \times 10^{-3}$M-perchloric acid. Below 230 mμ., small discrepancies were observed, but here the absorption due to the nitrate ion becomes considerable, and it was not possible to take measurements below 220 mμ., even at the full slit width of 2 mm.

Deviations from Beer's Law.—In an attempt to extend the analytical use of optical-density determinations to concentrations lower than 3×10^{-6}M-mercurous perchlorate, the dependence of log $(I_0/I)_{236 \cdot 5}$ on mercurous perchlorate concentration was investigated over the concentration range 5×10^{-6}—5×10^{-8}M., a cell of optical length 5 cm. being used. The solutions were made by successive dilutions from a solution $5 \cdot 10 \times 10^{-5}$M. in mercurous perchlorate and $1 \cdot 04 \times 10^{-2}$M. in perchloric acid. The concentration of the latter solution was checked by measuring its

optical density at 236·5 mμ. in a 1-cm. cell. Measurements were made at $1·04 \times 10^{-2}$M- and at $1·04 \times 10^{-3}$M-perchloric acid (treated with silver perchlorate) and each was repeated with completely new solutions. Agreement between the four sets of measurements was within experimental error. The average values of the optical density at 236·5 mμ. plotted against the concentration are shown in Fig. 1, curve *B*. Fig. 3 shows the plot of $(\varepsilon_{obs.})_\lambda$ against λ for solutions of mercurous perchlorate concentration $5·80 \times 10^{-5}$M. (1-cm. cell), $5·10 \times 10^{-6}$M., and $1·02 \times 10^{-6}$M., severally. The perchloric acid concentration was $1·04 \times 10^{-3}$M.

Various factors were considered in an attempt to account for the observed deviations from Beer's law at 236·5 mμ. and for the anomalous character of the $(\varepsilon_{obs.})_\lambda$–λ plots at different concentrations.

(1) Atmospheric oxidation of the mercurous ion does not appear to be responsible, as the optical density of the solutions remained constant over periods in excess of those required to make a complete set of optical measurements. (2) Adsorption of the mercurous ion on the walls of the vessels and cells used could cause deviations from Beer's law similar to those observed,

FIG. 3.
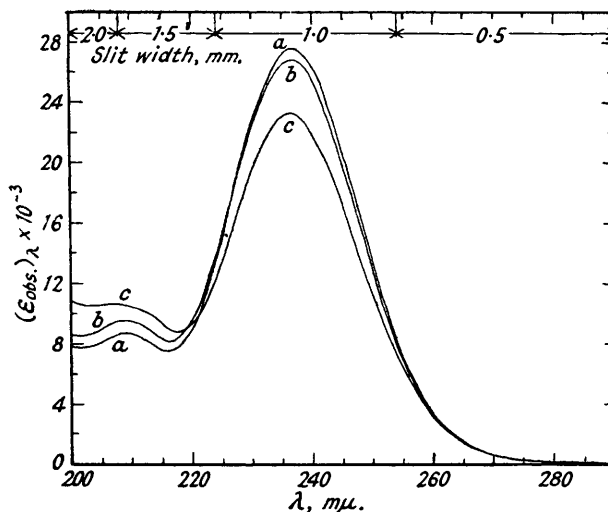
(a) $5·80 \times 10^{-5}$M-Hg$_2$(ClO$_4$)$_2$ (1-cm. cell).
(b) $5·10 \times 10^{-6}$M-Hg$_2$(ClO$_4$)$_2$ (5-cm. cell).
(c) $1·02 \times 10^{-6}$M-Hg$_2$(ClO$_4$)$_2$ (5-cm. cell).
[HClO$_4$] = $1·04 \times 10^{-3}$M.

but does not lead to a satisfactory explanation of the change in shape of the molecular extinction curves. (3) The establishment of the equilibrium $Hg_2^{++} \rightleftharpoons Hg^{++} + (Hg)_{liq.}$ would lead to linear rather than curved plots of optical density against concentration, and it is doubtful on energetic grounds whether the corresponding equilibrium involving mercury atoms could occur to an appreciable extent. (4) Impurities capable of reacting with mercurous ions and present in the perchloric acid solutions used for dilution could account for the effects observed. Such impurities are unlikely to be present in the silver perchlorate-treated, concentrated perchloric acid, as good agreement was found between measurements in which the perchloric acid concentrations differed ten-fold. The only remaining source seems to be the distilled water used; but samples distilled on different occasions were used with concordant results.

(5) The explanation adopted as most probable is that of an increasing finite degree of dissociation of the dimeric mercurous ion with decrease in total mercurous concentration. If this is the case, the larger values for $(\varepsilon_{obs.})_\lambda$ for the $1·02 \times 10^{-6}$M-mercurous perchlorate solution at wave-lengths less than 220 mμ. imply that at these wave-lengths the molecular extinction coefficient of the Hg$^+$ ion is comparable in magnitude with that of Hg$_2^{++}$. Thus even at 236·5 mμ. the contribution of the Hg$^+$ ions present to the total absorption may be significant in the most dilute solution. Comparison of the values of

$$\left(\frac{\varepsilon_{obs.}, \ c = 1·02 \times 10^{-6}\text{M.}}{\varepsilon_{obs.}, \ c = 5·80 \times 10^{-5}\text{M.}} \right)_\lambda$$

at different values of λ (Fig. 4) shows that there is an approximate constancy over the range $\lambda = 245$—254 mμ., and here this ratio reaches a minimum, 0·82. The possibility that here there is a similar functional dependence of ε_{Hg^+} and $\varepsilon_{Hg_2^{++}}$ on λ seems unlikely. It appears more probable that óver this wave-length range the absorption due to Hg$^+$ is negligible, and in any case there must be a finite absorption due to the monomeric ion at 236·5 mμ. (At wave-lengths greater than 254 mμ. an increase in this ratio is noticeable, but here the experimental error on the $(\varepsilon_{obs.})_\lambda$ values becomes large, *e.g.*, the value of the optical density at a concentration of $1·02 \times 10^{-6}$M. is only 0·016 at 260 mμ.) On the assumption that the degree of dissociation in the $5·80 \times 10^{-5}$M-solution is small

$$\left(\frac{\varepsilon_{obs.}, c = 1·02 \times 10^{-6} \text{M.}}{\varepsilon_{obs.}, c = 5·80 \times 10^{-5} \text{M.}}\right)_{245-254} = 1 - \alpha$$

where α is the degree of dissociation in the $1·02 \times 10^{-6}$M-solution. Hence

$$K_{diss.} = \frac{[\text{Hg}^+]^2}{[\text{Hg}_2^{++}]} = \frac{2^2(1 - 0·82)^2(1·02 \times 10^{-6})^2}{(0·82)(1·02 \times 10^{-6})} = 1·6 \times 10^{-7}$$

From this approximate value the degree of dissociation in $5·80 \times 10^{-5}$M-mercurous perchlorate is about 0·02, and so the plot of $(\varepsilon_{obs.})_\lambda$ against λ for this concentration is virtually the molecular extinction curve of the dimeric mercurous ion.
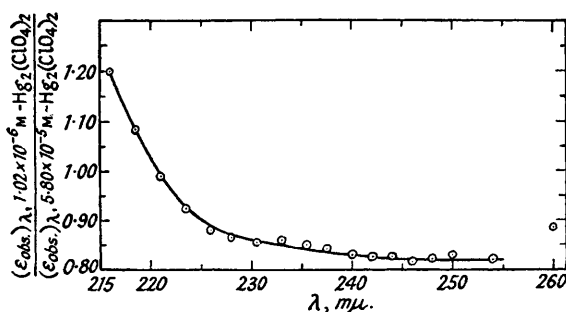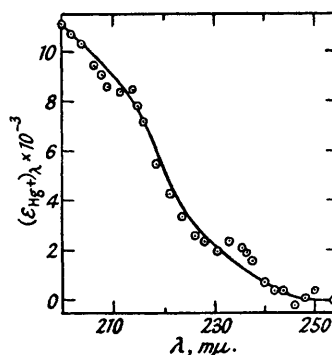
FIG. 4.

FIG. 5.

In $1·02 \times 10^{-6}$M-mercurous perchlorate the concentration of Hg$_2^{++}$ is $8·4 \times 10^{-7}$M., and of Hg$^+$ $3·7 \times 10^{-7}$M. Subtraction from the log $(I_0/I)_\lambda$ values for $1·02 \times 10^{-6}$M-mercurous perchlorate of the log (I_0/I) values for $8·4 \times 10^{-7}$M. " pure " dimer (calculated from the molecular extinction coefficients obtained from the $5·80 \times 10^{-5}$M-solution) gives the optical density due to $3·7 \times 10^{-7}$M-Hg$^+$ ion, and Fig. 5 shows the corresponding molecular extinction curve. Owing to the comparatively small differences between the two sets of figures, and to the approximations made, Fig. 5 gives at best only a semi-quantitative representation of the true molecular extinction curve for Hg$^+$.

To decide if the shape of the observed plot of log $(I_0/I)_{236·5}$ against mercurous perchlorate concentration (Fig. 1, curve *B*) is consistent with the approximate $K_{diss.}$ value obtained above, curves have been constructed for various values of $K_{diss.}$ by using the expression

$$\log (I_0/I)_{236·5}/l = (\varepsilon_{Hg_2^{++}})_{236·5} \times [\text{Hg}_2^{++}] + (\varepsilon_{Hg^+})_{236·5} \times [\text{Hg}^+]$$

[Hg$_2^{++}$] and [Hg$^+$] are related to [Hg$_2$(ClO$_4$)$_2$] through the dissociation constant $K_{diss.}$. The value of $(\varepsilon_{Hg^+})_{236·5}$ has been taken as 10^3 (Fig. 5) in all cases, log $(I_0/I)_{236·5}$ being comparatively insensitive to values of $(\varepsilon_{Hg^+})_{236·5}$ from zero to 2×10^3 except at the low concentration end of the plots, where the experimental accuracy is rather low. Appropriate values of $(\varepsilon_{Hg_2^{++}})_{236·5}$ have been calculated from the average value of $(\varepsilon_{obs.})_{236·5}$ over the range $5·10 \times 10^{-5}$— $3·0 \times 10^{-6}$M-mercurous perchlorate, the corresponding assumed value of $K_{diss.}$ being used. Fig. 6 shows the calculated curves for various $K_{diss.}$ values from 10^{-8} to 10^{-6}, and also the observed curve of optical density against total mercurous perchlorate concentration. The observed curve most nearly agrees with that calculated for $K_{diss.} = 10^{-7}$, and the general shape of the two curves is similar. The most obvious discrepancies occur at the very low concentrations, though here the values of both log $(I_0/I)_{236·5}$ and [Hg$_2$(ClO$_4$)$_2$] were subject to greater experimental error.

It seems probable therefore that the deviations from Beer's law, which become apparent only below about 10^{-6}M-mercurous perchlorate, can be ascribed to the maintenance of the equilibrium $Hg_2^{++} \rightleftharpoons 2Hg^+$ with a value of $K_{diss.} = [Hg^+]^2/[Hg_2^{++}]$ of the order of 10^{-7} mole per litre. This value is very approximate, but $K_{diss.}$ probably lies within the limits 10^{-6} and 10^{-8}.
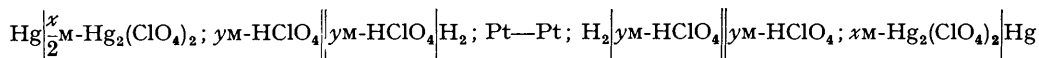
No experimental value for $K_{diss.}$ appears to have been reported previously, though Cartledge (*J. Amer. Chem. Soc.*, 1941, **63**, 906) has calculated ΔG for the dissociation of the dimeric ion in aqueous solution as $+42$ kcals. per mole, leading to a value of $K_{diss.}$ of 10^{-31}. On the other hand, Kolthoff and Barnum (*ibid.*, 1940, **62**, 3061) conclude from polarographic evidence that in concentrations of the order 10^{-20}M., mercurous mercury is almost completely in the form Hg^+. The smallest value of $K_{diss.}$ consistent with this observation is 10^{-18}.

Ogg's concentration-cell potential measurements (*Z. physikal. Chem.*, 1898, **27**, 285), although adequate to show the essentially dimeric character of mercurous mercury in concentrations

Fig. 6.
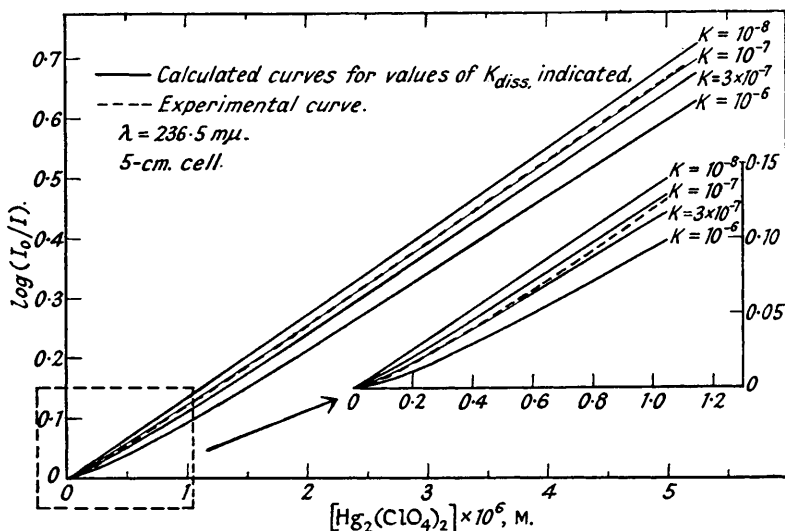
from 5×10^{-5} to 10^{-1}M., are not of sufficient accuracy to enable a calculation of $K_{diss.}$ to be made. Linhart (*J. Amer. Chem. Soc.*, 1916, **38**, 2356) has measured the potential of concentration cells of the type

$$Hg \left| \frac{x}{2}M\text{-}Hg_2(ClO_4)_2 \; ; \; yM\text{-}HClO_4 \right\| yM\text{-}HClO_4 \left| H_2 \; ; \; Pt\text{---}Pt \; ; \; H_2 \right| yM\text{-}HClO_4 \left\| yM\text{-}HClO_4 \; ; \; xM\text{-}Hg_2(ClO_4)_2 \right| Hg$$

and for values of $[Hg_2(ClO_4)_2]$ of $5\cdot031 \times 10^{-5}$M. and $1\cdot062 \times 10^{-4}$M., severally, gives a potential of $0\cdot0089$ volt, the theoretical value for a bivalent ion. The equilibrium dissociation of Hg_2^{++} at these concentrations, with a value of $K_{diss.}$ as high as 10^{-6}, would affect the observed potential by $0\cdot3$ millivolt only, of the order of the experimental error. This work does, however, establish 10^{-6} as an upper value of $K_{diss.}$. The value of pK of 7 ± 1 is thus consistent with the scanty experimental data available elsewhere, though no confirmation of this figure is forthcoming.

The use of concentration cells employing lower concentrations of mercurous perchlorate than 5×10^{-5}M. seems in principle to be the most suitable way of obtaining the dissociation constant, and it is hoped to use this method in an attempt to improve on the accuracy of the value suggested above.

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