THESIS

presented for the

M.Sc DEGREE

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UNIVERSITY OF LONDON

by Miss M. Barr.

ABSTRACT OF THESIS.

An investigation of the nature of Chlorauric acid and its potassium salt, has been carried out, with the object of ascertaining certain properties of the complex ions present in aqueous solutions of these compounds.

1.   The normal potential $Au|AuCl_4$ was determined at $25^{\circ}C$. by measuring the potential of gold electrodes in solutions containing a known concnetration of the complex compound, in the presence of a measured excess of chloride ions. The values of the normal potential were calculated from the equation,

$$E_h = {}_oE_h + \frac{RT}{3F} \ln \frac{[AuCl'_4]}{[Cl']^4}$$ where the symbols have

their usual meaning.

The mean values of ${}_oE_h$ were found to be 1.0066 volts and 1.0055 volts at 25°, from measurement of the acid and salt respectively. The value of this constant previously determined by Bjerrum and Kirschner is 1.001 volts at $17^{\circ}C$.

2.   The formulae of the complex ions existing in solutions containing different concentrations of the complex compound, in the presence of varying excess of chloride ions, were calculated by the method of Bodländer.

The results obtained indicate that the complex $AuCl'_4$ is the stable ion in solutions containing 0.1, 0.02 and 0.01 $\underline{M}$ chlorauric acid, in the presence of 0.1 $\underline{N}$ hydrochloric acid. With greater concentration of the latter, the higher complex $AuCl''_5$ is poduced, whilst in dilute solutions containing a small proportion of free chloride ions, hydrolysis occurs.

The ion $AuCl'_4$ preponderates in solutions of 0.02 $\underline{M}$

potassium chloraurate containing 0.02 and 0.04 $\underline{M}$ potassium chloride: no evidence was obtained, for the existence of higher complexes in solutions of this compound.

3.   The stability constant of the aurichloride ion,

$$K = \sqrt[3]{\frac{[AuCl_4^!]}{[Au^-][Cl^!]^4}}$$

was determined from E.M.F. measurements, from the results of which the concentration of auric ions was calculated, in solutions containing known concentrations of both the complex compound and free chloride ions.

The mean values obtained were 1.83×10^6 and 2.085×10^6, from measurements of solutions of Chlorauric acid and Potassium chloraurate respectively.

These values, together with the figures obtained for the normal potential Au|AuCl$_4^!$, shew that the complex ion AuCl$_4^!$ is somewhat less stable in the presence of hydrogen ions than in the presence of potassium ions of equivalent concentration.

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MOLLIE BARR.

"AN INVESTIGATION OF THE NATURE OF
CERTAIN COMPLEX GOLD COMPOUNDS IN
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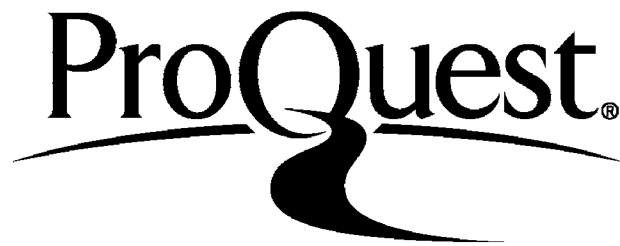
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An Investigation of the Nature of Certain

Complex Gold Compounds in Aqueous Solution.

Part I   -   Introduction.

A review of the literature relating to gold compounds
shews that very few of the numerous complex derivatives of
this metal have been studied in solution, by Physico-chemical
methods. An investigation of certain complex derivatives of
Auric chloride, namely Chlorauric acid and its Potassium salt,
has therefore been carried out, with the object of ascertaining
the nature of the complex ions present in aqueous solution,
and the stability of these ions in the presence of a measured
excess of chloride ions.

Both the structure of complex compounds in the solid
state and the stability of their ions in solution, are of
interest in connection with theories of Co-ordination and
Atomic structure. The relative stability of complex ions, how-
ever, is also of great importance in a number of technical
processes for the preparation of pure metals. The stability of
a complex ion is greater the less it tends to decompose into
its constituents, and the less it tends to unite with one con-
stituent to form higher complexes, and certain complex salts
have/shewn to exhibit very great stability in aqueous solution.
been
Such compounds behave as simple salts, giving rise only to ions
of two kinds, the concentration/simple ions formed by
                              of

decomposition being very small or negligible. The
difference between double and complex ~~ie~~ salts is however,
of degree rather than kind, since double salts have been
shewn to give rise to a small concentration of complex ions
in all but the most dilute solutions. Similarly, complex
salts in solution contain a small concentration of all the
constituent simple ions, the proportion of which increases
on dilution. Intermediate between these two types of salts
come such compounds as the ferrioxalates, which in solution,
give rise to ferric, oxalate and ferrixalate ions in suffi-
cient concentration to give positive qualitative tests. A
complex salt is therefore commonly regarded as a salt which
in solution, dissociates to give such inappreciable concen-
tration of simple ions as cannot be detected by a qualitative
test.

The nature of complex ions is usually investigated by
Electrochemical methods, and the method most generally adopted
is due to Bodländer (Dedekind Festschrift, Braunschweig. 151.
1901) who first studied the silver-ammonium cation (Bodländer
and Fittig. Z. Physik. Chem. 39 597. (1902)). This investi-
gation was concerned with the compounds formed by union of
certain silver salts with ammonia, and the results shewed that
the complex ion is represented by the formula $(Ag(NH_3)_2$. A
similar conclusion was drawn by Euler (Ber. 36 1854. 2878 (1903),
who investigated the nature of the bases formed by combination

of silver oxide with ammonia and with methylamine. The following
important investigations on complex salts may be enumerated.

Bodländer and Eberlein (Z.anorg.Chem $\underline{39}$ 197 (1904)
examined the complex salts produced by dissolving silver iodide,
cyanide and thiocyanate in solutions of the corresponding pot-
assium salt, and shewed that all three compounds give rise to a
series of complex ions. Thus, in the case of Potassium silver iodide,
the results obtained lead to the conclusion that molecules $K_2Ag_2I_4$

$K_3Ag_2I_5$; $K_4Ag_2I_6$; $K_5Ag_2I_7$ exist together in equilibrium, the higher
compounds preoponderating in solutions of high Potassium iodide con-
tent. In addition to these, the presence of $K_3Ag\ I_4$ was detected in
concentrated solutions. In solutions of the complex cyanide in which
the concentration of free anion is less than 0.05 $\underline{N}$, the complex
ion is represented by the formula $Ag(CN)_2^{\underline{1}}$; with higher concentration
of cyanide ions however, the complex $Ag(CN)_3^{\underline{11}}$ is produced, the stabi-
lity constants of the two ions being of the same order of magnitude.
Similar results were obtained for the complex thiocyanate.

Of the Cuprous salts which have been investigated, the
most interesting are Potassium cuprocyanide (Kunschert.Z.anort.Chem.
$\underline{41}$. 1. 359. (1904)) and the corresponding cupro-chloride and -bromide
Bodländer and Storbeck(Z.anorg.Chem. $\underline{31}$ 458.(1902).The results indi-
cate that anions of the type $CuX_2^{\underline{1}}$ and $CUX_3^{\underline{11}}$ exist in such solutions;
in the case of the cuprocyanide, the limiting concentration of free

cyanide ions corresponding to the complex $Cu(CN)_2^!$ is undefined, whilst in the case of potassium cuprochloride the compound $K-CuCl_2$ predominates in solutions in which the KCl-concentration is between 0.1 and 0.22 $\underline{N}$, K_2CuCl_3 existing in solutions of higher chloride content.

In contrast to the behaviour of these silver and cuprous compounds, potassium aurocyanide (Bodländer, Ber. $\underline{36}$ 3933. (1903) and potassium aurothiocyanate (Bjerrum and Kirschner D.Kgl. Videnskabernes Selskab 8 $\underline{v}$. 1. (1918)) exhibit no measurable tendency to unite with excess cyanide and thiocyanate ions respectively. In all the solutions which have been invest- igated, ions of the type $AuX_2^!$ alone have been detected, even in the presence of a large excess of the alkali salt. Examination of solutions of Potassium aurithiocyanate (Bjerrum and Kirschner- loc.cit.) has indicated that the complex ion exists mainly as the tetrathiocyanate $Au(SCN)_4^!$. The ordinary method of invest- igation, however, was found to be inapplicable in the case of this compound, and a method involving the measurement of oxidation potentials, was employed. Spectrophotometric exam- ination of certain solutions gave an indication of the exist- ence of higher complexes.

An investigation of the complex thiosulphates of cadmium, lead, thallium, nickel, iron and zinc, with sodium thiosulphate, (Euler, Ber. $\underline{37}$. 1704. (1904)) shewed that these compounds are of a very unstable order. This small tendency to complex

formation is especially evident in the zinc, nickel and ferrous compounds.

Among other zinc compounds, the following are of interest:- Sodium zincate, $NaHZnO_2$, and ammonium zinc oxalate (Kunschert. Z. anorg. Chem. 41. 337 (1904)). The former ionises to give only one type of complex ion, $HZnO_2^-$, the stability of which is comparatively low. The latter, however, dissociates with the formation of the ions $Zn(C_2O_4)_2''$ and $Zn(C_2O_4)_3''''$ of which the lower complex is present in solutions of free oxalate concentration less than 0.1 N, and the higher ion in solutions of greater oxalate concentration.

Potassium mercuricyanide (Bodländer. Ber. 36 3933. (1903), Abegg and Sherrill, Z.Elektrochem. 9 549. Z.Physik. Chem. 43 705. (1903)) is an extremely stable salt, dissociating in solution to form $2K^{\cdot}$ and $Hg(CN)_4''$ ions. Abegg and Sherrill, however, have demonstrated the existence of the ion $Hg(CN)_3^{!}$ in solutions saturated with mercuric cyanide. The values of the stability constants of the $Hg(CN)_4''$ ion, as calculated by these investigators and by Bodländer, are in very close agreement.

The results of these investigations shew that complex compounds fall into two groups:-

1. Those which are stable in the presence of an excess of the free anion contained in the complex.

2. Those which unite with excess of the free anion to

form a series of complex ions.

The first group is examplified by Potassium aurocyanide, potassium aurothiocyanate, sodium zincate and potassium mercuricyanide. Most other complex compounds belong to the second class.

Method of Investigation.

The formula and stability constants of complex ions in aqueous solution, may both be obtained from the result of Electromotive Force measurements. The application of Bodländer's method is best described by means of an example.

Supposing the aurocyanide ion to have the formula $Au_m(CN)_n$, the values of m and n/m may be determined by measurement of two types of concentration cell, in both of which gold electrodes are used. The value of m is obtained from the E.M.F. of a cell, both halves of which contain the same known excess of potassium cyanide, but different concentrations of the complex gold compound. Values of n/m, on the other hand, are determined from the E.M.F. of cells in which the concentration of complex salt in each half cell is the same, while the amount of free potassium cyanide is varied.

The two types of cell may be represented as follows:-

1.   Au | Complex KCN | KCN Complex / Au
               x c c y

2.   Au | Complex KCN | KCN Complex | Au
              c_1 x y c_1

Since all complex ions undergo some measure of decom-

position into their simple constituents, the following
equilibria exist in each half cell -

$$(Au_m(CN)_n)_1 \rightleftharpoons m(Au')_1 + n(CN')_1 \text{ on the left hand side,}$$

$$(Au_m(CN)_n)_2 \rightleftharpoons m(Au')_2 + n(CN')_2 \quad \text{''} \quad \text{'' right '' ''}$$
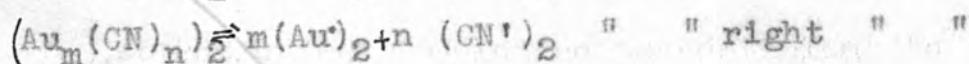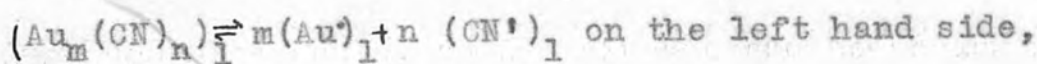
$$\therefore \quad [Au']_1^m [CN']_1^n = k [Au_m(CN)_n]_1$$

similarly $[Au']_2^m [CN']_2^n = k.[Au_m(CN)_n]_2$

Thus, eliminating k by division,

$$\frac{[Au_m(CN)_n]_1}{[Au_m(CN)_n]_2} = \frac{[Au']_1^m [CN']_1^n}{[Au']_2^m [CN']_2^n}$$

or

$$\frac{[Au']_1^m}{[Au']_2^m} = \frac{[Au_m(CN)_n]_1 . [CN']_2^n}{[Au_m(CN)_n]_2 [CN']_1^n} \quad \text{-----------------(1)}$$

The E.M.F. of a concentration cell, (neglecting liquid
contact potentials) constructed with gold electrodes in sol-
utions of aurous ions, is given by,

$$E = \frac{RT}{F} \ln \frac{[Au']_1}{[Au']_2} \quad \text{the electrode (1) being the positive pole.}$$

Substituting from equation (1)

$$E = \frac{RT}{F} \ln \frac{[Au_m(CN)_n]_1 [CN']_2}{[Au_m CN_n]_2 [CN']_1}$$

For a cell of the first type in which the concentration
$[CN]_1 = [CN]_2$.

$$E = \frac{RT}{F} \ln \left\{ \frac{[Au_m(CN_n)]_1}{[Au_m(CN_n)]_2} \right\}^{\frac{1}{m}}$$

Thus, $m = \frac{RT}{FE} \ln \frac{[Au_m(CN_n)]_1}{[Au_m(CN_n)]_2}$

In the second type of cell, the concentration of complex is the same in each half cell, and

$$E = \frac{RT}{F} \ln \frac{[CN']_2}{[CN']_1}$$

or,

$$n/m = \frac{E.F.}{RT \ln \frac{[CN']_2}{[CN']_1}}$$

Thus, by calculation of the values of the m and n/m, the formula of the complex ion is obtained.

The application of these equations involves the assumptions that the complex compound is (a) completely ionised, and (b) not appreciably hydrolysed, in the soltions investigated. The degree of dissociation of the salt cannot be measured, since dilution of solutions of complex compounds causes progressive decomposition of the complex ion: the value of the conductivity at infinite dilution therefore has no definite meaning, and the salt must be assumed to be completely ionised. This assumption can only reasonably be justified in moderately dilute solutions, which do not contain a large excess of any compound producing a common ion. By simple hydrolysis of a complex compound, is understood the decomposition of the compound into its constituent simple ions, in solution: this occurs to some small extent with all complexes. Many salts however, are composed of an insoluble and a soluble constituent, and therefore such hydrolysis as occurs is negligible, since any appreciable decomposition would cause precipitation of the insoluble constituent. Thus, the assumption that no important

hydrolysis occurs, is justified in the case of compounds made up of one insoluble component, but cannot be justified when applied to complexes formed by union of two soluble compounds. The degree of such hydrolysis as may occur, if of the simple type described above, may be obtained by measurement of the concentration of the free ion, metallic or nonmetallic, liberated by decomposition of the complex ion. This concentration may be calculated from the results of Electromotive Force measurements.

The work of Kohlrausch on Conductivity (Z.Physik.Chem. 33 287. (1900) of Hittorf and Salkowsky (Z.Physik.Chem.28 546 (1899)) on Transport numbers, has indicated that another type of hydrolysis occurs in solutions of certain complex compounds of this kind. Thus solutions of Chlorauric acid undergo hydrolysis with the production of a hydroxy complex, according to the equation,

$$Au\ CL_4' + H_2O \rightleftharpoons AuCl_3\ OH' + H^{\cdot} + Cl'$$

Similarly there is evidence that dilute solutions of Chloroplatinic acid are hydrolysed under the influence of light.

The degree of hydrolysis of Chlorauric acid in 0.1 $\underline{M}$ solution, was calculated by Bjerrum and Kirschner loc.cit). Their method consisted in measuring the potential of a gold electrode in the solution, and the amount hydrolysed, x, was calculated from the equation,

$$E = {}_oE + \frac{RT}{3F} \ln \frac{[AuCl_4]}{[Cl']^4} \qquad \text{where} \begin{array}{l} [AuCl_4] \\ \hline [Cl'] \end{array} = \begin{array}{l} 0.1\,(1-x) \\ 0.1\,x \end{array}$$

$${}_oE = \text{normal potential Au} \mid AuCl_4$$

The value of ${}_oE$ was calculated from the above equation using values of E for solutions containing a known concentration of Chlorauric acid in the presence of a known excess of hydrochloric acid.

From the value of x so obtained, the hydrolysis constant was calculated, and the percentage hydrolysis of 1 M and 0.01 M solutions. The following results were obtained,

    1 M solution 0.74% 0.1 M 6.9% 0.01 M 45%

Determination of Stability Constants.

The stability constant of a complex ion is given by the nth root of the Mass Action Constant for formation of the complex from its constituent simple ions, where n is the valency of the metal concerned.

Thus the stability Constant for the aurocyanide ion, $Au(CN)_2$ is $K = \dfrac{[Au(CN)_2]}{[Au'][CN']^2}$

and for the $Hg(CN)_4''$ ion, $K = \sqrt{\dfrac{[Hg(CN)_4'']}{[Hg][CN']^4}}$ since two atoms of univalent gold are required to replace one atom of bivalent mercury.

The value of K may be determined by measurement of the concentration of free metallic ions in a solution containing a known concentration of the complex compound in the presence of

a known excess of one of its simple constituents. Thus the
stability constant for the ion $Ag(CN')_2$ may be determined
by measuring the potential of silver in a solution of known
$Ag(CN)_2^!$ and cyanide-concentration, and calculating the con-
centration of free silver ions by means of Nerust's equation.
The value of the electromotive force may also be used for the
calculation of the normal potential $Ag|Ag(CN)_2^!$ where

$$E = {_oE} \frac{RT}{F} \ln \frac{[Ag(CN)_2^!]}{[CN']^2} \qquad \text{The values of such normal potentials}$$

give an indication of the relative stability of two complex
ions containing the same metal but different negative radicles.
The ratio of the stability constants of the aurocyanide and
aurothiocyanate ions, was calculated by Bjerrum and Kirschner
(loc.cit).

$$K = \frac{[Au(SCN)_2^!]}{[Au'][SCN']^2} \qquad\qquad K' = \frac{[Au(CN)_2^!]}{[Au'][CN']^2}$$

$${_oE} - {_oE'} = \frac{RT}{F} \ln \frac{K'}{K} \quad \text{where} \quad {_oE} = \text{normal potential}$$
$$Au|Au(SCN)_2$$
$$= 0.689 \text{ volts.}$$
$${_oE'} = \text{normal potential}$$
$$Au|Au(CN)_2^!$$
$$= 0.611 \text{ volts.}$$

$$\ln \frac{K'}{K} = \frac{{_oE} - {_oE'}}{\frac{RT}{F}}$$

$$\frac{K'}{K} = 10^{\frac{0.689-(-0.611)}{0.058}} \qquad\qquad = 10^{22.4}$$

i.e. the stability constant of the aurocyanide ion is
$10^{22.4}$ times that of the aurothiocyanate ion.

The stability constant of the aurocyanide ion is stated

by Bodländer (loc.cit) to be in excess of 2.5×10^{29}, and

this is the highest value found for any complex ion so far

investigated. The uncertainty in the value is due to a lack

of an accurate knowledge of the normal potential Au|Au'. Values

of K have been determined for a number of other complex ions,

and the figures calculated vary within very wide limits, from

the value quoted above for the aurocyanide ion, to 1.9×10^{3}

for the complex $Zn(C_2O_4)_2''$

The present investigation of Chlorauric acid and

Potassium chloraurate was therefore carried out, to determine

such propoerties of the aurichloride ion as have been discussed

in relation to other complex ions, and to compare the results

obtained with those found from investigation of similar compounds.

Part II   -   Experimental.

Preparation of Chlorauric Acid.

The Chlorauric acid required in the investigation, was prepared by dissolving pure gold in a mixture containing two parts by volume, of concentrated hydrochloric acid and one part of concentrated nitric acid. The excess nitric acid remaining after complete solution of the metal, was expelled, as far as possible, by boiling, after which the liquid was filtered, treated with dilute hydrochloric acid and water, and evaporated to crystallisation. The yellow needles so obtained exhibit deliquescent properties and solutions of definite known concentration cannot be prepared by direct weighing. Solutions of approximately the required strength were therefore prepared, and analysed gravimetrically by reduction to metallic gold.

Preparation of Potassium Chloraurate.

Potassium chloraurate was prepared by dissolving a known weight of pure gold in aqua regia, and after removal of the excess nitric acid by boiling, evaporating the solution in the presence of the theoretical quantity of potassium chloride. The crystals were finally placed in a vacuum desiccator over quicklime, to remove possible traces of hydrochloric acid.

As in the case of Chlorauric acid solutions of approxi-

mately the required strength were prepared, and analysed
by the same method.

Method of Analysis.

The gold solutions were analysed by reduction with
oxalic acid. Precipitation of the metal proceeds extremely
slowly in the cold, but much more rapidly when the solutions
are heated. In the early stages of the investigation, con-
siderable difficulty was experienced owing to the frequent
production of comparatively stable colloidal solutions:
this tendency, however, was later much reduced by heating the
solution of the gold compound nearly to boiling, with oxalic
acid, and slowly adding sodium hydroxide. In these circum-
stances, it was found that the gold was immediately preci-
pitated in small glittering particles, which coalesced on
boiling. The solutions, when completely decolourised, were
filtered, and the precipitates washed free from soluble
oxalates and chlorides, dried and ignited in the usual manner.

Electromotive Force Measurements.

The Electromotive Force measurements were performed
by the Compensation method, using a direct reading slide-wire
Potentiometer, reading to 0.1 millivolt. A sensitive moving
coil galvanometer was used as zero instrument, the spot of
light from the illuminated mirror being projected on to a
scale placed at a distance of 1 metre from the galvanometer.
A Weston normal element was employed as standard cell. All

the Potential measurements were conducted at 25°C. Half
cells of the usual type, but of reduced dimensions, were
used, and gilded platinum loops were employed as electrodes.
The platinum wires were gilded by cathodic deposition from
a dilute solution of potassium auricyanide, using small
currents.

I. Investigation of the Nature of the Aurichloride
Ion in Solutions of Chlorauric Acid.

(a)   Determination of the Normal Potential $Au | AuCl_4'$

The value of the normal potential $Au | AuCl_4'$ was
determined by measuring the potential of gold electrodes in
solutions containing a known concentration of Chlorauric
acid in the presence of a known excess of hydrochloric acid.
A decinormal ccalomel electrode was used as standard half-
cell, and saturated potassium chloride in the middle vessel.

The values of the normal potential $_0E_h$, were cal-
culated from the equation -

$$E_h = {}_0E_h + \frac{RT}{3F} \ln \frac{[AuCl_4']}{[Cl']^4} ,$$ the application of this

formula involving the assumption that the potential is a
measure of the reaction $AuCl_4' + 3\varepsilon = Au^{...} + 4Cl'$. The results
of the measurements of eleven different solutions, shew that
this equation represents the reaction, though the values of

$_o E_h$ shew slight deviations from one another. The greatest difference in the values amounts to 15 millivolts.

A series of similar measurements of this acid, was performed by Bjerrum and Kirschner (loc.cit) with the object of determining the relative stabilities of the aurichloride, and aurithiocyanate ions. The measurements were conducted at 17°C., using a decinormal calomel electrode as standard half cell, and saturated potassium chloride in the middle vessel. The solutions examined consisted of 0.1 $\underline{M}$ H $AuCl_4$ in the presence of varying concentrations of free hydro-chloric acid. These investigators experienced difficulty in obtaining constant values of the electromotive force, and attributed the variation to a possible equilibrium between aurous and auric ions. The maximum difference between their values amounted to 23 millivolts.

In the present investigation, however, no difficulty was experienced except when dealing with solutions of con-centration 0.02 $\underline{M}$ H $AuCl_4$, and more dilute. These solutions were found to be chemically unstable, and shewed a tendency to deposit gold on the walls of the electrode vessel. In the case of solutions of concentration 0.01 $\underline{M}$ H $AuCl_4$ containing a small excess of free hydrochloric acid, decomposition pro-ceeded so rapidly as to permit of only one reliable measure-ment.

Liquid Contact Potentials.

The liquid contanct potential at the junction Calomel

electrode | sat. KCl was, being very small, neglected in the calculations.

The values of the potential at the boundary H AuCl$_4$, HCl| sat. KCl, are unknown. Although a considerable amount of work has been done, with the object of measuring the potential at the junction of saturated solutions of potassium chloride and solutions of hydrochloric acid of various concentrations, the values obtained by different investigators do not lead to the same conclusion. The results of such investigations before 1923, are discussed by G. Scatchard (J.Amer.Chem. Soc. 45 1716. (1923)), who concludes that the liquid potential between saturated potassium chloride and solutions of hydrochloric acid more dilute than 0.1 N, is not more than one millivolt, but that the value increases rapidly with concentration of hydrochloric acid.

Fales and Vosburgh (J.Amer.Chem.Soc.40 1291.(1918)) concluded, from the results of their own experiments, that Planek's formula is inapplicable to this pair of solutions, and further state that the contact potential in the case of hydrochloric acid of concentration 0.1 - 1.0 N is zero.

In agreement with this, Aten and van Dalfsen (Rec.trav. chim. 45 177. (1926)) conclude from the results of a similar investigation, that saturated potassium chloride eliminates contact potentials between 1.0 and 0.1 and between 0.1 and 0.01 N HCl solutions.

Owing to the uncertainty in the different values, it was decided, in the present investigation of Chlorauric acid, to accept the results of Aten and van Dalfsen and Pales and Vosburgh. The values of the liquid contact potential saturated $KCl \mid HAuCl_4, HCl$, have therefore been taken as zero for all the solutions examined, since the range of concentration of free hydrochloric acid in these solutions lies between 0.01 and 1 - Normal.

The results of the measurements are given in Table I.

Table I.

Solution.							
				E		E_h	$_oE_h$
$HAuCl_4$	HCl	α	1	2	3	(mean)	
0.1	0.1	93%	0.7275	0.7274	0.7278	1.0690	1.0070
0.1	0.2	90.5	0.7041	0.7031		1.0450	1.0059
0.1	0.5	84.0	0.6744	0.6746		1.0159	1.0058
0.02	0.02	96.8	0.7609	0.7607		1.1022	1.0000
0.02	0.04	95.6	0.7475	0.7473		1.0888	1.0150
0.02	0.1	93.0	0.7170	0.7164		1.0581	1.0100
0.02	0.2	90.5	0.6891	0.6888		1.0304	1.0052
0.01	0.01	98.0	0.7821	0.7820		1.1235	1.0038
0.01	0.02	96.8	0.7574			1.0988	1.0039
0.01	0.05	95.0	0.7344			1.0758	1.0105
0.01	0.1	93.0	0.7064	0.7062		1.0477	1.0055

Mean value of $_oE_h$ = 1.0066 volts

The first column of the table gives the molecular concentration of Chlorauric and hydrochloric acid in each

solution, and the second column the value of the degrees of dissociation of the latter at $25^{o}C$. In the third column are values of the E.M.F. of the cell Au|Solution|saturated KCl| 0.1NKCl₁Hg₂Cl₂|Hg and under E_h the mean value of the single potential referred to the hydrogen standard. These figures were obtained by addition, to the mean of the values of column III, of 0.624, the factor representing the E.M.F. of the decinormal calomel electrode at $25^{o}C$. subtraction of 0.2826 converts the values obtained to the hydrogen standard. The calculated Normal Potential values are given in the last column, the mean of the figures being 1.0066 volts as compared with 1.001 volts (Bjerrum and Kirschner) for $17^{o}C$.

Determination of the Formula of the Complex Ion.

The formula of a complex ion as stated in Part I, is determined from values of the E.M.F. of two types of concentration cell. Inthis investigation, in order to simplify the measurements, each half of the concentration cell was measured against a decinormal calomel electrode, certain systems being combined when the potentials became constant, and re-measured as check. An example is given in Table II a.

Table II a.

Solution		E.M.F against	E.M.F. of concentration.	E.M.F. of concentration.
HAuCl$_4$	HCl	calomel electrode	Cell(by calculation)	cell (measured)
0.02	0.04	0.7473	0.0309	0.0308
0.02	0.1	0.7164		

Table II contains the results of measurements of
concentration cells in which each half cell contains the same
concentration of Chlorauric acid, the amount of free hydro-
chloric acid in each half being different. In this Table,
the concentration of Chlorauric acid in the solutions, is
given in Column I. Columns 2 and 4 give the concentration
of excess hydrochloric acid in each half cell, and under
α_1 and α_2 are the degrees of dissociation of the hydrochloric
acids 1 and 2 respectively. In the sixth column are values
of the E.M.F. of the concentration cells, calculated from the
figures obtained for each half cell, and under $n/_m$ the ratio
of the number of chlorine atoms to the number of gold atoms
contained in the complex ion Au$_m$Cl$_n$. These values were calcu-
lated from the equation $N/_m = \dfrac{3\,E}{0.0595 \log \dfrac{[Cl']_2}{[Cl']_1}}$ the derivation

of which is discussed in Part I.

Table II

Con.of Complex	$[HCl]_1$	α_1	$[HCl]_2$	α_2	E	n/m
0.1	0.1	93.0%	0.2	90.5%	0.0240	4.18
0.1	0.1	93.0	0.5	84.0	0.0351	4.08
0.1	0.2	90.5	0.5	84.0	0.0291	4.01
0.02	0.02	96.8	0.04	95.6	0.0134	2.28
0.02	0.02	96.8	0.1	93.0	0.0441	3.26
0.02	0.02	96.8	0.2	90.5	0.0718	3.72
0.02	0.04	95.6	0.1	93.0	0.0307	4.01
0.02	0.04	95.6	0.2	90.5	0.0584	4.36
0.02	0.1	93.0	0.2	90.5	0.0277	4.83
0.01	0.01	98.0	0.02	96.8	0.0246	4.20
0.01	0.01	98.0	0.05	95.0	0.0477	3.50
0.01	0.01	98.0	0.1	93.0	0.0757	3.91
0.01	0.02	96.8	0.05	95.0	0.0230	2.97
0.01	0.02	96.8	0.1	93.0	0.0511	3.78
0.01	0.05	95.0	0.1	93.0	0.0281	4.85

Table III contains the results of measurements of concentration cells of the other type, in which the concentration of excess hydrochloric acid is the same in each half cell, the quantity of Chlorauric acid being varied

Table III

Conc.of Free HCl	Conc. of Complex I	Conc. of Complex II	E	m
0.02	0.02	0.01	0.0034	1.74
0.05	0.05	0.01	0.0137	1.01
0.1	0.1	0.01	0.0213	0.93 mean
0.1	0.1	0.02	0.0109	1.26 1.1
0.2	0.1	0.02	0.0146	0.95
1.0	0.1	0.01	0.0145	1.35

The second and third columns give the concentration
of Chlorauric acid in each half cell, and the amounts of free
hydrochloric acid in each, is given in column 1. The last
column gives values of m, the number of gold atoms in the com-
plex ion, calculated from the equation,

$$m = \frac{0.0595}{3 E} \log \frac{[AuCl_4']_1}{AuCl_4'{}_2}$$

c) Determination of the Stability Constant for the
Aurichloride Ion.

The results of the determination of the formula
of the aurichloride ion, indicate that the complex ion is
representated by $AuCl_4'$ in solutions of gold concentration
0.01 and 0.02 and 0.1 containing 0.1N HCl. The values of
the potential of gold electrodes in these solutions , are
therefore used to calculate the Stability constant of the
$AuCl_4'$ ion.

Stability constant $= K \quad =3\sqrt{\dfrac{[AuCl_4^{\,\prime}]}{[Au^{\cdots}][Cl^{\prime}]^4}}$

Owing to the absence of reliable data concerning the value of the normal potential $Au|Au^{\cdots}$ at $25^{\circ}C.$, the stability constant of the aurichloride ion cannot be calculated with any great degree of accuracy. The normal potential $Au|Au^{\cdots}$ has been accurately determined at $18^{\circ}- 19^{\circ}C$, by Jirsa and Jelinck (Z.Elektrochem. 30 534. 286.(1924)) who measured the potential of gold in electrolytically-prepared solutions of auric sulphate and nitrate. The value of $_oE_h$ was found to be $+1.39$ volts from consideration of the sulphate, and $+1.37$ volts from measurements of the nitrate.

In order to determine the approximate order of magnitude of the Stability constant for the aurichloride ion, the mean of these values for $18^{\circ} - 19^{\circ}C$, was used in the calculation.

Evaluation of the Stability Constant.

1.   Single potential $Au\left|\begin{smallmatrix} HAuCl_4 \\ 0.1 \end{smallmatrix}\right.\begin{smallmatrix} HCl \\ 0.1 \end{smallmatrix} = 1.0690$ volts

referred to the hydrogen standard.

$\therefore 1.0690 - 1.38 \dfrac{0.0595}{3}$ log.c where c = conc. of free auric ion

$$\text{whence} \quad c = 2.085 \times 10^{-16}$$

$$K^3 = \frac{0.1 \times 10^{16}}{2.085 \times (0.093)^4}$$

$$= 6.413 \times 10^{18}$$

$$\therefore \quad K = 1.86 \times 10^6$$

2)   Single Potential $Au|HAuCl_4$ HCl $= 1.0581$ volts.

$0.02$0.1

$\thereforec = 5.888 \times 10^{-17}$

$$K^3 = \frac{0.02 \times 10^{17}}{5.888 \times (0.093)^4}$$

$$= 4.54 \times 10^{18}$$

Whence
$$K = 1.66 \times 10^6$$

----

3)   Single Potential $Au|HAuCl_4$ HCl $= 1.0477$ volts.

$0.01$0.1

$\thereforec = 1.762 \times 10^{-17}$

$$K^3 = \frac{0.01 \times 10^{17}}{1.762 \times (0.093)^4}$$

$$= 7.587 \times 10^{18}$$

Whence
$$K = 1.965 \times 10^6$$

Since the normal potential $Au|Au^{\cdots}$ should have a higher value at 25° than at $18^\circ C$, the mean value of K, 1.83×10^6, is probably slightly low. The calculation serves to prove, however, that the aurichloride ion has no great stability in aqueous solution.

II Investigation of the Nature of the Aurichloride
Ion in Solutions of Potassium Chloraurate.

Solutions of Potassium Chloraurate were investigated by exactly similar methods to those described for Chlorauric acid. The excess chloride ions were provided by addition of potassium chloride of known concentration, in place of hydrochloric acid used in the previous experiments. The liquid contact potentials at the boundary of the solutions and saturated potassium chloride, being very small and unknown, were neglected.

The values of the normal potential $Au|AuCl_4$ are given in the last column of Table IV.

Table IV.

Solution		α	E.M.F. against decinormal calomel			E_h	$_oE_h$
$KAuCl_4$	KCl	for KCl	1	2	3	mean	
0.1	0.1	86.1%	0.7372	0.7374		1.0787	1.0107
0.1	0.2	82.0	0.7085	0.7093		1.0503	1.0078
0.1	0.5	78.26	0.6746	0.6744		1.0159	1.0034
0.02	0.02	92.1	0.7670	0.7661		1.1080	1.0040
0.02	0.04	89.7	0.7438	0.7431		1.0849	1.0038
0.02	0.1	86.1	0.7163	0.7169		1.0580	1.0072
0.02	0.2	82.0	0.6918	0.6921		1.0334	1.0048
0.02	0.5	78.26	0.6665	0.6668		1.0080	1.0093
0.01	0.01	94.1	0.7785	0.7795		1.1204	0.9993
0.01	0.02	92.1	0.7602	0.7611		1.1021	1.0041
0.01	0.05	86.9	0.7314	0.7322		1.0732	1.0056
0.01	0.1	86.1	0.7081	0.7089	0.7099	1.0503	1.0055

Mean value of $_oE_h$ = 1.0055

The mean value of the normal potential was found to be 1.0055 volts, as compared with 1.0066 volts, obtained from measurements of Chlorauric acid. In the case of Potassium chloraurate, the numerical difference between the highest and lowerest values of $_oE_h$, amounts to 11.4 millivolts.

Table V contains the results of measurements of concentration cells, of which each half contained the same concentration of chlorauric acid, the amount of excess potassium chloride being varied.

Table V

Conc. of KAuCl$_4$	$[KCl]_1$	α_1	$[KCl]_2$	α_2	E	n/m
0.1	0.1	86.1%	0.2	82%	0.0284	5.11
0.1	0.1	86.1	0.5	78.26	0.0628	4.83
0.1	0.2	82.0	0.5	78.26	0.0334	4.61
0.02	0.02	92.1	0.04	89.7	0.0230	4.01
0.02	0.02	92.1	0.1	86.1	0.0500	3.76
0.02	0.02	92.1	0.5	78.26	0.1000	3.79
0.02	0.04	89.7	0.5	78.26	0.0769	3.72
0.02	0.1	86.1	0.5	78.26	0.05000	3.83
0.01	0.01	94.1	0.02	92.1	0.0183	3.16
0.01	0.01	94.1	0.05	88.9	0.0473	3.53
0.01	0.01	94.1	0.1	86.1	0.0701	3.67
0.01	0.02	92.1	0.05	88.9	0.0289	3.81
0.01	0.02	92.1	0.1	86.1	0.0517	3. 90
0.01	0.05	88.9	0.1	86.1	0.0228	4.02

The concentration of Potassium chloraurate in each solutions is given in column 1, and the amount of free potassium chloride together with the degree of dissociation in columns II to V. The last column contains the values calculated for n/m, the ratio of the number of chlorine to the number of gold atoms in the complex ion.

Table VI contains the results of measurements of concentration cells of the other type, from which values

of m, the number of gold atoms in the complex, have been calculated.

Table VI.

Conc. of KCl($\underline{N}$)	Conc. of KAuCl$_4$		E	m
	1	2		
0.02	0.02	0.01	0.0059	1.01
0.1	0.02	0.01	0.0077	0.78
0.1	0.1	0.01	0.0284	0.70
0.1	0.1	0.02	0.0207	0.67
0.2	0.1	0.02	0.0169	0.82
0.5	0.1	0.02	0.0080	1.73
1.0	0.1	0.02	0.0111	1.26
4.15(Satd.)	0.02	0.01	0.0046	1.30
4.15 "	0.1	0.01	0.0153	1.30
4.15 "	0.1	0.02	0.0107	1.30

Mean = 0.72 (for the rows with m = 0.78, 0.70, 0.67)

Evaluation of the Stability Constant for the Aurichloride Ion.

An approximate value of the stability constant was calculated as in the case of Chlorauric acid, using the value of the normal potential Au|Au$^{...}$ determined at 18° - 19°C.

The solutions considered in the calculation were those containing 0.02 $\underline{N}$ KAuCl$_4$ in the presence of 0.02 and 0.04 $\underline{N}$ KCl, since the complex ion in these solutions is represented by the formula AuCl$_4^-$

1.   Single potential $Au | KAuCl_4, KCl = 1.1080$ volts
                               0.02 0.02

      referred to the hydrogen standard.

$$1.1080 = 1.38 \quad \frac{0.0595}{3} \quad \log c$$

$$c = 1.932 \times 10^{-14}$$

$$K^3 = \frac{0.02 \times 10^{14}}{1.932 \times (0.02 \times 0.921)^4}$$

$$= 8.99 \times 10^{18}$$

whence $K = 2.08 \times 10^6$

2)   Single potential $Au | KAuCl_4, KCl = 1.0849$ volts
                               0.02 0.04

$$1.0849 = 1.38 \quad \frac{0.0595}{3} \quad \log c$$

$$c = 1.321 \times 10^{-15}$$

$$K^3 = \frac{0.02 \times 10^{15}}{1.321 \times (0.04 \times 0.897)^4}$$

$$= 9.13 \times 10^{18}$$

whence $K = 2.09 \times 10^6$

III Attempt to Measure the degree of Hydrolysis

of Solutions of Chlorauric acid and Potassium Chloraurate.

An attempt was made to measure the chloride ion con-
centration of certain solutions of Chlorauric acid and potassium
chloraurate, with a view to obtaining the degree of hydrolysis,
which proceeds according to the equation,

$$AuCl_4' + H_2O \rightleftharpoons AuCl_3 \, OH' + H' + Cl'$$
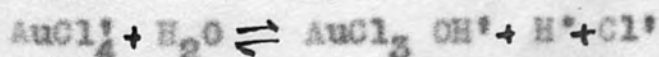
The Ag - AgCl electrode was used, but the experiments
were unsuccessful, owing to reduction of the solution by the
silver, which became gilded.

The Chemical Instability of Solutions.

Solutions of Chlorauric acid of concentration less
than 0.1M, were found to be unstable, and nearly all such
solutions decompose to some extent with separation of metallic
gold. The stability of the solutions is increased by the in-
troduction of hydrochloric acid, but in 0.01 M concentration
of Chlorauric acid, at least 0.1N HCl is required to prevent
decomposition within a few days of preparation. Some doubt is
therefore entertained as to the accuracy of the values of the
potential obtained for 0.01 M solutions containing a concen-
tration of hydrochloric acid below 0.1 N.

The solutions of potassium chloraurate were found to
be comparatively stable, though the more dilute solutions
shewed a tendency to deposit a small quantity of metallic
gold. The instability in both instances may be attributed to
the existence of an unstable hydrolytic product, since decom-
position occurs in dilute solution and in those solutions
containing small or no excess of free chloride ions.

Part III   - Summary and Discussion of Results.

Chlorauric Acid.

The low value of the Stability constant of the
Aurichloride ion, as well as the high value of the normal
potential $Au|AuCl_4'$, shew that this complex ion has a small
stability in aqueous solution; a result which is supported
by the numerical values of m and $n/_m$. These are in no sense
constant, varying with both the concentration of the complex
acid, and that of the hydrochloric acid. Generally, the
value of m increases with increasing concentration of free
chloride ions, the figures obtained for solutions containing
0.05, 0.1 and 0.2 $\underline{N}$ hydrochloric acid being approximately
unity.

The values of $n/_m$ obtained from E.M.F. measurements
of 0.1 $\underline{M}$ chlorauric acid solutions, decrease with increasing
concentration of hydrochloric acid. This decrease, which is
very small, may be attributed to a driving back of the ioni-
sation of the Chlorauric acid in the presence of a large
excess of hydrogen ions.

For the purpose of comparison, the results of Bjerrum
and Kirschner's measurements at 17°C, have been used to calcu-
late values of $n/_m$ in 0.1 $\underline{M}$ solutions. Their results shew
that $n/_m$ decreases with increasing concentration of hydrochloric
acid, but the decrease in this case is much larger. A comparison
of the two sets of results is given in Table VII.

Table VII.

N.Bjerrum and A.Kirschner.				M.Barr.			
$[HCl]_1$	$[HCl]_2$	E	n/m	$[HCl]_1$	$[HCl]_2$	E	n/m
0.1	0.25	0.037	5.13	0.1	0.2	0.0240	4.18
0.1	0.5	0.060	4.65	0.1	0.5	0.0351	4.08
0.25	0.5	0.023	4.05	0.2	0.5	0.0291	4.01

These figures in the third and fourth columns are calculated from Bjerrum and Kirschner's results. Their values permit of the calculation of a single figure for m, namely 0.31, obtained from measurements of solutions containing respectively 0.05 and 0.1 $\underline{M}$ $HAuCl_4$ in the presence of 0.5 $\underline{N}$ hydrochloric acid. While the values of n/m indicate the existence of an ion $AuCl_5''$, the abnormally low figure obtained for m suggests a considerable hydrolysis in the more dilute solution.

It is therefore taken from the results of the present investigation, that the complex ion exists in 0.1 $\underline{M}$ solutions as the tetrachloride ion $AuCl_4'$, the mean value of m for solutions containing 0.1 $\underline{N}$ HCl, being 1.1.

In the 0.02 $\underline{M}$ solutions, the values of n/m given in Table II, shew progressive increase with increasing concentration of hydrochloric acid, from 2.28 to 4.83, the value 4.01 being obtained from potential measurements of solutions containing 0.04 and 0.1 $\underline{N}$ hydrochloric acid. Since the

value of m in solutions containing 0.1 $\underline{N}$ HCl, is 1.1 the complex ion in the solutions 0.02 $\underline{M}$ HAuCl$_4$, 0.1 $\underline{N}$ HCl, and 0.02 $\underline{M}$ HAuCl$_4$, 0.04 $\underline{N}$ HCl, probably exists almost entirely as the AuCl$_4'$ ion. The abnormally low values obtained from measurements of solutions of small chloride concentration, indicate that the latter is present in unsufficient quantity to suppress hydrolysis of the complex. The values obtained for solutions containing high concentration of hydrochloric acid, point to the existence of an ion AuCl$_5''$.

Consequently it may be taken that in the presence of a high concentration of hydrochloric acid the complex ion is present as AuCl$_5''$, but at lower concentrations, AuCl$_4'$ is the stable ion: this, at still lower concentrations, rapidly dissociates to less chlorinated ions which are so unstable that their presence cannot be established from the E.M.F. measurements.

The values of n/m obtained from measurements of 0.01 $\underline{M}$ solutions (Table II) exhibit fluctuations. These variations may in part be attributed to the unstable nature of certain of the solutions. The value obtained from consideration of solutions containing 0.05 and 0.1 $\underline{N}$ hydrochloric acid, supplies additional evidence of the existance of an ion of constitution AuCl$_5''$.

The results therefore indicate that the aurichloride ion in solution of Chlorauric acid, resembles the aurithio-

cyanate ion, but the investigations of Bjerrum and Kirschner
shew that the latter has a Stability Constant $10^{17.7}$ times
that of the former at 17°C.

Potassium Chloraurate.

The value of the normal potential Au|AuCl$_4$ calculated
from the results of measurements of potassium chloraurate
solutions, furnishes additional evidence of the comparative
instability of the aurichloride ion. The value 1.0055 volts
was determined as mean, from these measurements, and it is
in close agreement with 1.0066 volts, the value obtained from
the investigation of Chlorauric acid. The mean value of K,
the stability constant of the complex ion, is somewhat higher
for potassium chloraurate than for Chlorauric acid, the figures
obtained being 2.085 x 10^6 and 1.83 x 10^6 for the salt and
acid respectively. The slightly lower value of $_oE_h$ and higher
value of K, obtained in the case of potassium chloraurate,
indicate that the stability of the aurichloride ion is slightly
greater in the presence of potassium ions than in the presence
of hydrogen ions of equivalent concentration.

The values of m, as in the case of Chlorauric acid,
tend to increase with increasing concentration of free chloride
ions. The values of n/m, however, exhibit irregularities, and
in 0.1 M solutions (Table V) shew progressive decrease with
increasing concentration of potassium chloride. Since no
difficulty was experienced in obtaining constant values of the

E.M.F. of the cells concerned, it may be taken that the equation used to calculate n/m, is not strictly applicable to the case of the comparatively concentrated solutions. Since the use of the equation involves the assumption that the complex salt is completely ionised, this explanation is probably correct, for it is highly improbable that the degree of dissociation of 0.1 $\underline{M}$ KAuCl$_4$ would be either complete, or identical in solutions containing 0.1, 0.2 and 0.5 - normal potassium chloride.

The results of measurements of 0.02 $\underline{M}$ potassium chloraurate solutions (Tables V and VI) demonstrate that the complex ion exists entirely as the tetrachloride ion in solutions containing 0.02 and 0.04 $\underline{N}$ potassium chloride. The values of n/m obtained from consideration of these solutions is 4.01 and the figure for m in solutions containing 0.02 $\underline{N}$ KCl is 1.01. But in the case of solutions containing a higher concentration of potassium chloride, values of n/m have been found, which are approximately constant and somewhat less than 4: hence it follows that the complex ion is present chiefly as AuCl$_4'$.

The data obtained from the measurement of 0.01 $\underline{M}$ solutions, indicate that hydrolysis occurs in solutions of low potassium chloride concentration. The values 3.90 and 4.02 however, furnished respectively by measurements of solutions containing 0.02 and 0.1 $\underline{N}$ KCl, and 0.05 and 0.1 $\underline{N}$KCl, again shew that the ion AuCl$_4'$ is present.

<u>Values of m for Potassium Chloraurate.</u>

The values of m obtained for Potassium chloraurate
shew, with a few exceptions, progressive increase with in-
creasing concentration of free potassium chloride. The ex-
perimentally determined values of $n/_m$ point to unity as the
most probably figure for m, and great significance is not at-
tached to the quantities calculated from experiment. Calcu-
lation of this factor involves the assumption that the complex
salt is completely ionised in solution. This is unjustifiable,
and moreover the relative influence of potassium chloride on
the degree of ionisation of potassium chloraurate in two sol-
utions of different concentration, is unknown and cannot be
regarded as being identical for both solutions. Thus the
ratio $\dfrac{[AuCl_4']_1}{[AuCl_4']_2}$ referring to two solutions containing

respectively 0.1 and 0.01 $\underline{M}$ $KAuCl_4$, may be numerically equal
to, less than or greater than ten. Thence for all cases,
where m is actually unity, it will follow that where the exper-
mental value of m is less than one, the potassium chloride has
a greater depressing effect on the ionisation of the complex in
the more dilute than the more concentrated solution. Where the
experimental value of m is greater than unity, the ionisation
of the complex is depressed more in the more concentrated than
in the more dilute solution. The value 1.01, obtained from the
E.M.F. of the cell Au | 0.02 $\underline{M}$ $KAuCl_4$ $0.^02$ $\underline{N}$ KCl $\dashv$ 0.02 $\underline{N}$ KCl,

0.01 $\underline{M}$ $KAuCl_4$ | Au is regarded as trustworthy, since the concentrations of both potassium chloride and potassium chloraurate are small, and the presence of the former would be expected to have no very different effect on the degree of ionisation of the latter in either of the solutions.

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