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On the Complex Chemistry of the Uranyl Ion

I. The Hydrolysis of the Six-valent Uranium in Aqueous Solutions

STEN AHRLAND

Department of Inorganic and Physical Chemistry, Chemical Institute, University of Lund, Lund, Sweden

The six-valent uranium ion U^{6+} does not exist at all in aqueous solution. Even in the most acid solutions, the uranyl ion UO_2^{2+}, which we may regard as a hydrolysed state of U^{6+}, is exclusively formed. Thus the only compound ever prepared that may be considered as a salt of U^{6+}, the uranium fluoride UF_6, is immediately and completely transformed into UO_2F_2 by water (Ruff and Heinzelmann [1]). The uranyl ion is then the only form of existence for six-valent uranium over a wide pH-range up to pH $\approx$ 2.5. If pH is raised over that value base is consumed, however, and further hydrolysis occurs (see *e. g.* Britton [2]). From such solutions »basic uranyl salts» have been prepared (see *e. g.* Colani [3]). Finally, at sufficiently high pH, insoluble uranate precipitates are formed.

Thus the uranyl group UO_2^{2+} forms a stable atom constellation, which behaves in a manner completely analogous to other metal ions: it keeps unchanged within wide acid pH-limits, and as pH further increases, it gradually is subjected to a hydrolysis more and more pronounced.

These are the current views as to the range of existence and hydrolysis of the uranyl ion. As an introduction to the extensive investigation of the complex chemistry of the ion, which is in progress, an independent test of their truth seemed to be highly desirable. This was performed in extinctiometric way, as follows. In such a test, as in all investigations where the properties of just the uranyl ion is to be determined, it is, of course, necessary to use a non-complex salt in the measurements. As such, the perchlorate has been selected.

Determination of the $[H^+]$-range where the six-valent uranium is found as uranyl ions only

The following extinction curves have been obtained photographically by two Hilger Medium Spectrographs one of which, with quartz prism, was used in the ultra violet, and the other, with glass prism, in the visible range where quartz gives a bad dispersion. They have been combined with a Hilger Spekker Photometer, graduated directly in extinctions E. About the measuring method, see Twyman and Allsopp[4] or Kortüm[5].

According to Beer, we have for a solution of a light absorbing substance

$$\log J_0/J = E = \varepsilon_0 \cdot C_0 \cdot d \qquad (1)$$

where
J_0 = light intensity entering, and
J = light intensity leaving the absorbing layer
d = thickness of layer
C_0 = concentration of absorbing substance, and
ε_0 = the molar extinction, a constant characteristic of the substance at a given wave-length.

If several light absorbing substances are present in the same solution, E is put together additively:

$$E/d = \varepsilon_0 \cdot C_0 + \varepsilon_1 \cdot C_1 + \varepsilon_2 \cdot C_2 + \ldots . \qquad (2)$$

This is the case in a light absorbing complex system; ε_0, ε_1, $\varepsilon_2 \ldots$ are then the molar extinctions and C_0, C_1, $C_2 \ldots$ the concentrations of the different components of the complex equilibrium.

In such cases, we know the total concentration of central atom, C_M, free as well as complexly bound. We may quite formally attribute E to this total concentration; *i. e.* we define a quantity ε_M according to

$$E/d = \varepsilon_M \cdot C_M \qquad (3)$$

This quantity is always experimentally determinable.

ε_M so defined becomes identical to ε_0 in the limiting case where only one component exists, but in all other cases it is a formal quantity of calculation; t forms a sort of mean between the ε values of the different components, and ts value depends obviously upon the mutual proportions of the component concentrations. How much it varies as these proportions are altered to a certain extent, depends, of course, on the differences between the ε values. At a separate wave-length these differences may by chance be small, and so no appreciable changes in ε_M occur by changes in the composition of the system. But in all probability this cannot be the case at all wavelengths; thus, if a displacement of an equilibrium occurs, ε_M is to change at least at one part of an extinction curve. On the other hand, we may state, that no appreciable equilibrium displacement has happened in such a case where a whole extinction curve has remained unchanged. This method to prove complex formation in a solution is in its first origin due to Bjerrum[6].

In the present case, the aim is to settle at which $[H^+]$ displacements of hydrolytic equilibria take place in uranyl solutions. So extinction curves have been determined for uranyl perchlorate at different $p[H^+]$* values: 0.1, 0.6, 1.0, 1.55, 2.7 and 4.1. The lower $p[H^+]$ values have been obtained by adding $HClO_4$, the higher by adding NaOH. The former have been calculated from the acid added, the latter by quinhydrone electrode measurements according to the method described below. The $p[H^+]$ values need not to be known but roughly.

As in all following measurements, a high and approximately constant ionic strength $I = 1$ has been maintained in the solutions, to secure constant activity conditions as far as possible. $NaClO_4$ has been used as ionic medium. All measurements have been made at 20° C. The chemicals used are the same as in the main series (see below).

The extinction curves found are given in Fig. 1. From $p[H^+]$ 0.1 (the lowest investigated one where the whole ionic medium is $HClO_4$) up to $p[H^+]$ 1.55, the courses are completely identical within the limits of the experimental error $\pm$ 2—3 %**. Thus no appreciable equilibrium displacement has occurred between these $p[H^+]$ values. According to the law of mass action, this result does not allow any other interpretation than that one hydrolysed state predominates over the whole of this $p[H^+]$ range. This hydrolysed state must be the uranyl ion, UO_2^{2+}. At $p[H^+]$ 2.7, however, a distinct deviation is found. Hence UO_2^{2+} begins to be perceptibly hydrolysed. At still higher $p[H^+]$ (4.1), in the neighbourhood of beginning precipitation, this deviation is very strongly pronounced.

One may, however, also imagine a non-hydrolytic complex reaction to take place in uranyl solutions: a polymerisation, forming $(UO_2)_2$, $(UO_2)_3 \cdots (UO_2)_n$. As such a formation is unaffected by $[H^+]$, its existence does not be-

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* $p[H^+] = -\log [H^+]$.

** Corresponding to ± 0.01 log units.

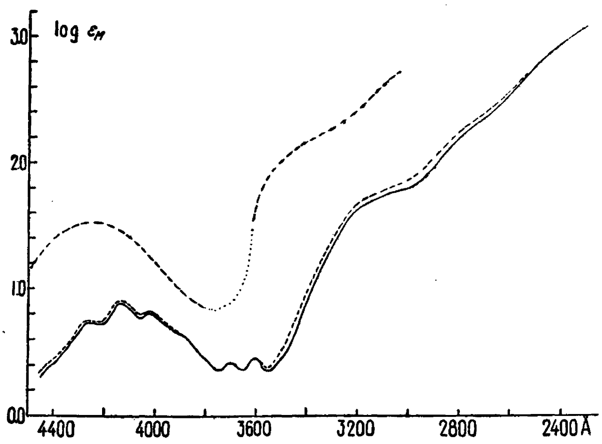

Fig. 1. Extinction curves of uranyl perchlorate solutions. — Fulldrawn curve: $p[H^+] = 0.1$ *to* 1.55 (= *extinction curve of the uranyl ion,* UO_2^{2+}). — *Dashed curves:* $p[H^+] = 2.7$ *(lower curve) and* $p[H^+] = 4.1$ *(upper curve).*

come evident by pH variations. On the other hand, according to the law of mass action, displacements should take place in this case, when C_M is varied. Now identical curves are obtained at p[H$^+$] 0.6 when $C_M \approx 40$ mC while d varies, and when $d = 2$ cm while C_M varies between 2.5 mC and 176 mC. From this the conclusion is to be drawn, that no polymers are formed.

So it is unambiguously shown that the monomer uranyl ion is the only ionic specie of uranium existing in perchlorate solutions in the p[H$^+$] range 0.1—1.55. At higher p[H$^+$] values further hydrolysis occurs. Thus the current views have been well confirmed.

Then it is evident, that the fulldrawn curve may be identified as the extinction curve of the uranyl ion, that is for this curve $\varepsilon_M = \varepsilon_0$. As far as I know this is the first carefully verified absolute determination of this subject.

In a great number of old investigations the absorption of several more or less complex uranyl salts was qualitatively determined. Quantitative extinction curves of uranyl perchlorate have, on the other hand, only been measured by v. Kiss *et al.*[7, 8] and by Sutton [9]. v. Kiss *et al.* have published two highly different versions, none of them in accord with mine. Sutton has only measured the range down to 3400 Å. In this, he finds curves of the same shape and pH dependence as I, but no absolute values of extinction were communicated.

The existing possibilities of complex formation in solutions of uranyl salts

After having fully proved that UO_2^{2+} is to be regarded as a stable complex forming central group, we may treat its complex chemistry in complete agreement with that of other metal ions. Thus in a solution of uranyl salt we have to count with the following possible complexes between the central group M ($= UO_2^{2+}$) and a ligand A, if the polymers M_2 etc are excluded, according to the above:

Mononuclear:	MA, MA_2, MA_3, ...
Dinuclear:	M_2A, M_2A_2, M_2A_3, ...
m-nuclear:	M_mA, M_mA_2, M_mA_3 ....

We know the total concentrations of M and A:

$$C_M = [M] + [MA] + [MA_2] + \ldots . + 2([M_2A] + [M_2A_2] + \ldots) + \ldots .. \\ + m([M_mA] + [M_mA_2] + \ldots) + \ldots \quad (4)$$

$$C_A = [A] + [MA] + 2[MA_2] + \ldots + [M_2A] + 2[M_2A_2] + \ldots + [M_mA] + 2[M_mA_2] + \ldots \quad (5)$$

As all solutions have an approximately constant ionic strength = 1, by $NaClO_4$, the law of mass action is valid for the connection of the complex concentrations with [M] and [A]. Generally we find for a complex M_mA_n:

$$[M_mA_n] = \beta_n^{(m)} \cdot [M]^m \cdot [A]^n \quad (6)$$

where $\beta_n^{(m)}$ is the n:th complex constant in the m-nuclear series. — Substituting these expressions in (4) and (5) we thus obtain C_M and C_A as functions of [M] and [A] only.

Of these two variables, one cannot measure [M] in an uranyl system; no practicable method is known. On the other hand, it is possible to find [A] in different ways. In such cases, the separation of the complex constants is done via the so-called complex formation curve (Bjerrum[10, pp. 21, 36], Olerup[11, p. 10], Fronaeus[12, p. 13]. Therefore the first step is to deduce its equation at the quite general complex formation, which is set forth here.

Deduction of the complex formation function

First we define a new quantity, the ligand number $\bar{n}$, according to

$$\bar{n} = \frac{C_A - [A]}{C_M} \quad (7)$$

that is the average number of complexly bound ligands per central atom; $\bar{n}$ is known as soon as [A] has been experimentally measured. $\bar{n}$, taken as a function of [A], is called the complex formation curve of the system in question. Its equation is obtained from (4) and (5) by substituting the expressions from (6) for the complex concentrations:

$$\bar{n} = \frac{\beta_1'[A] + 2\beta_2'[A]^2 + 3\beta_3'[A]^3 + \ldots. + [M](\beta_1''[A] + 2\beta_2''[A]^2 + 3\beta_3''[A]^3 + \ldots.) +}{1 + \beta_1'[A] + \beta_2'[A]^2 + \beta_3'[A]^3 + \ldots + 2[M](\beta_1''[A] + \beta_2''[A]^2 + \beta_3''[A]^3 + \ldots) +}$$

$$\frac{+ \ldots. + [M]^{m-1}(\beta_1^{(m)}[A] + 2\beta_2^{(m)}[A]^2 + 3\beta_3^{(m)}[A]^3 + \ldots.) + \ldots}{+ \ldots. + m[M]^{m-1}(\beta_1^{(m)}[A] + \beta_2^{(m)}[A]^2 + \beta_3^{(m)}[A]^3 + \ldots.) + \ldots} \quad (8)$$

If only mononuclear complexes exist in the solution, that is β'', β''', ..., $\beta^{(m)}, \ldots = 0$, it is seem from (8), that $\bar{n}$ is a function of [A] only, and independent of [M], On the other hand, if polynuclear complexes are formed, $\bar{n}$ is a function of both [A] and [M], that is C_M. Thus, by determining experimentally $\bar{n}$ as a function of [A] at different C_M, it is possible to decide between these two principal cases *.

This very important decision is the first thing to be done in every system to be investigated, since the treatment of (8) in order to separate the constants will depend on whether or not the terms from polynuclear complexes may be cut out. In these investigations, both cases have been met with and they will be treated as they become evident.

The hydrolysis as the first complex uranyl system investigated here

The further hydrolysis of UO_2^{2+} at p[H$^+$] exceeding ≈ 2.5 was selected as the first UO_2^{2+} system to be investigated, because the hydrolysis is to be considered at all other complex investigations of an ion in aqueous solution. For if hydrolysis complexes are formed to a considerable extent in addition to others in a solution of a salt, the conditions become so complicated that a quantitative interpretation is impossible. So it is, as a rule, quite necessary to reduce the concentrations of hydrolysis complexes to negligible amounts by performing

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* This is true as a rule. But as pointed out by Leden [13, p. 23], it may happen, that the criterion does not function; the polynuclear complexes then remain unknown. The very fact that $\bar{n}$ in such cases is independent of [M] allows us nevertheless to determine the correct mononuclear constants of the system in the usual way.

measurements in sufficiently acid solutions. That means, however, a limitation of the pH range available for complex measurements which for easily hydrolysed ions, as UO_2^{2+}, may be very considerable. Especially in such cases, the course of the hydrolysis is the central problem of the complex chemistry of an ion.

Previous work at the hydrolysis of UO_2^{2+}

Several investigations have been made in this field; the most prominent of the recent ones by Jolibois and Bossuet [14], Britton [2], Flatt and Hess [15], Sutton [9]. With the possible exception of Sutton's work, hardly any is of a quantitative character. The greatest interest has as a rule been devoted to the composition of the precipitates obtained by a large addition of base. As these are slimy and filter very badly and have a great tendency to adsorb and occlude, it is not surprising that the authors have got widely different results; especially as the composition certainly depends on the base quantity used.

Sutton measures pH (with glass electrode?) and light absorption (see above) of UO_2^{2+} solutions and finds that the hydrolysis includes formation of polynuclear complexes. However, the result is uncertain, as the author has not taken into account all the possibilities of complex formation; instead he has selected some complexes, the formation of which he finds plausible. A judgment of the work is also difficult for the reason that no information is given as to how the constants have been calculated.

The complexes and the complex formation function of the hydrolysed uranyl system

In the measurements, base is consumed, while UO_2^{2+} is transformed in a hydrolysed state. We may, therefore, quite formally regard the hydrolytic reactions as a complex formation between UO_2^{2+} as central group and OH^- as ligand. To this complex formation we may apply the scheme above, which covers all cases.

To what extent this view also corresponds to the actual facts cannot be decided. The measurements give, of course, no information at all about what really happens just in the moment of reaction, as only the resulting products is determined. Moreover, the degree of hydratation of these still remains unknown. So a complex, which according to the scheme is written $(UO_2)_2(OH)_2$ may equally well have a formula $(UO_2)_2O$, which gives the same equilibrium equation in this diluted aqueous solution.

It is possible to introduce a limitation in the scheme of complex formation, when used in this case. The co-ordination number of oxygen cannot exceed four, so a OH^--group cannot co-ordinate more than three UO_2^{2+}. Hence the m-nuclear serie begins with a complex $M_m(OH)_p$, where p depends on m.

By construction of formulas, we find $p = (m—1)/2$ if m is odd, and $p = m/2$ if m is even. Besides MOH; M_2OH and M_3OH thus are the only possible complexes with one OH^--group.

In the following experiments it is not our free ligand concentration $[OH^-]$, but $[H^+]$ which is the directly measured quantity. They are, however, connected according to $[OH^-] = K_W/[H^+]$. As the exact value of the constant K_W is not known for the ionic medium used, the values of $[OH^-]$ then become uncertain with a constant factor. Therefore, the direct measured $[H^-]$ is preferred as a variable in the complex formation function. By substituting $[OH^-] = K_W/[H^+]$ and conjoining the constants β and K_W to new constants $\varkappa$, which may be regarded as dissociation constants of UO_2^{2+}, we obtain from (6):

$$[M_mA_n] = [M_m(OH)_n] = \beta_n^{(m)}[M]^m[OH^-]^n = \beta_n^{(m)} \cdot K_W^n \cdot \frac{[M]^m}{[H^+]^n} = \varkappa_n^{(m)} \cdot \frac{[M]^m}{[H^+]^n} \tag{9}$$

and hence we obtain the complex formation equation (from (8)) as:

$$\bar{n} = \frac{1}{[H^+]} \cdot \frac{\left(\varkappa_1' + \frac{2\,\varkappa_2'}{[H^+]} + \frac{3\,\varkappa_3'}{[H^+]^2} + \ldots\right) + [M]\left(\varkappa_1'' + \frac{2\,\varkappa_2''}{[H^+]} + \frac{3\,\varkappa_3''}{[H^+]^2} + \ldots\right) + \ldots + [M]^{m-1}\left(\frac{p\varkappa_p^{(m)}}{[H^+]^{p-1}} + \frac{(p+1)\varkappa_{p+1}^{(m)}}{[H^+]^p} + \frac{(p+2)\varkappa_{p+2}^{(m)}}{[H^+]^{p+1}} + \ldots\right) + \ldots}{\left(1 + \frac{\varkappa_1'}{[H^+]} + \frac{\varkappa_2'}{[H^+]^2} + \ldots\right) + 2[M]\left(\frac{\varkappa_1''}{[H^+]} + \frac{\varkappa_2''}{[H^+]^2} + \frac{\varkappa_3''}{[H^+]^3} + \ldots\right) + \ldots + m[M]^{m-1}\left(\frac{\varkappa_p^{(m)}}{[H^+]^p} + \frac{\varkappa_{p+1}^{(m)}}{[H^+]^{p+1}} + \frac{\varkappa_{p+2}^{(m)}}{[H^+]^{p+2}} + \ldots\right) + \ldots} \tag{10}$$

where $\bar{n}$ means the average number of OH^-, used up per UO_2^{2+}, whatever the actual mechanism of complex formation may be. — We observe, that in the equation so modified, $\bar{n}$ is a function of $[H^+]$ only, if merely mononuclear complexes exist, but of both $[H^+]$ and $[M]$ (C_M) if polynuclear complexes exist, too.

The following measurements fully prove, that the hydrolysis doubtless involves polynuclear complex formation. So (10) is valid in the general form given above, and we will see how far this complicated function allows a separation of the constants.

Separation of constants from the complex formation curve of the hydrolysis system

Certainly it is quite impossible to completely determine the composition of the system for two weighty reasons:

1. The great number of possible complexes; and
2. the impossibility of measuring [M] $(=[UO_2^{2+}])$, present in (10). No known electrode measures [M] with the exception of the redox electrode UO_2^{2+}/U^{4+}, but according to Titlestad[16] this electrode is very slow to attain equilibrium; it is also light-sensitive. Moreover, one has to know the U^{4+}-complexity in the solution to be able to calculate [M]; but we do not.

We have to be content with a limited aim, and it proves to be possible to calculate the first mononuclear constant $\varkappa_1'$, and also the first dinuclear $\varkappa_1''$ defined according to (9). — We multiply both members of (10) by $[H^+]$. If we then allow $[H^+] \rightarrow \infty$ (that is $1/[H^+] \rightarrow 0$), simultaneously $\bar{n} \rightarrow 0$. The left member $\bar{n} \cdot [H^+]$ then tends toward a limit, which is easily obtained from the right member, if we bear in mind, that simultaneously also $[M] \rightarrow C_M$:

$$\lim_{1/[H^+] \rightarrow 0} \bar{n} \cdot [H^+] = \varkappa_1' + \varkappa_1'' \cdot C_M + \varkappa_1''' \cdot C_M^2 \qquad (11)$$

Thus, if the products $\bar{n} \cdot [H^+]$ are calculated from the experimentally found $\bar{n} = f([H^+])$ curves of different C_M so the products for increasing $[H^+]$ will tend towards the limits (11). If then the graphically estimated limits are plotted as a function of C_M, a curve ought to be obtained, the interception of which on the Y-axis is $= \varkappa_1'$; further the derivative in the point of section is $= \varkappa_1''$. At decreasing C_M, the curve better and better ought to be approximated by the straight line $\lim \bar{n} \cdot [H^+] = \varkappa_1' + \varkappa_1'' \cdot C_M$, which exactly means the equation of the tangent in the point of section.

Chemicals used

The *uranyl perchlorate* has been prepared according to Salvadori[17], with the modification, that the perchlorate solution first obtained has been reprecipitated and then dissolved again, to avoid traces of NO_3^-, which will disturb the analysis. The preparation contains some potassium perchlorate, which, of course, is of no importance here, since sodium perchlorate is used as ionic medium. — The stock solutions of uranyl perchlorate have been analysed volumetrically according to Treadwell[18]. The method works very well if no NO_3^- is present.

Sodium perchlorate. Preparations of the quality »purum» have been recrystallised twice from water of c:a 90° C, according to Fronaeus[12, p. 31]. Then the salt is obtained without water of crystallisation. Dried at 110°. The Cl^- and ClO_3^- contents are $< 1/10$ ‰

Perchloric acid, Mercks *pro analysi.* The stock solutions have been analysed by alkalimetric titration.

Sodium hydroxide. Stock solutions were prepared from oily alkali and thus free from CO_3^{2-}. The solutions used for titrations were analysed with potassium hydrogen phthalate as a standard.

Quinhydrone was prepared according to Biilman and Lund[19].

EXPERIMENTAL DETERMINATION OF THE COMPLEX FORMATION FUNCTION AT DIFFERENT C_M

The measurements for determination of $[H^+]$ have been carried out by

1. Quinhydrone electrode and
2. Glass electrode

The latter has been used as an independent control of the former.

The procedure has been the potentiometric titration used by Leden[13, p. 34]: known amounts of sodium hydroxide were added from a burette to uranyl perchlorate solutions of known concentration in the electrode vessel; all solutions used had the same ionic strength (= 1). The mixing of the measuring solutions was brought about by a stream of nitrogen gas. Every titration was repeated at least once.

The nitrogen gas had, to be released from the oxygen present, passed over copper of 200° C, finely divided on infusorial earth. After that, the gas was bubbled through a wash-bottle containing 1 C $NaClO_4$ to get the right pressure of aqueous vapour.

As a reference electrode (RE) in all measurements, a quinhydrone electrode of the composition

$$\text{Au}\left|\begin{array}{l}10.10\ \text{mC}\ \text{HClO}_4\\ 990\ \ \text{mC}\ \text{NaClO}_4\\ \text{quinhydrone (s.)}\end{array}\right.$$

was used, connected with the other half-cell by a salt bridge (written $||$), containing 1000 mC $NaClO_4$ (*cf.* Leden[13, p. 33]). — The experiments were made at 20.0° C in an electrically regulated thermostate.

As it is a very difficult task, if realizable at all, to obtain the extremely soluble uranyl perchlorate in the proper stoicheiometric proportions, one cannot get a defined starting condition simply by dissolving the salt in $NaClO_4$-solution. According to the accidental excess or deficit of acid in the preparations one finds different $[H^+]$ in such solutions and in no case that $[H^+]$, which corresponds to the spontaneous hydrolysis, *i. e.* the $[H^+]$ of the point of equivalence, $[H^+]_{eq}$:

$$[H^+]_{eq} = [MOH] + 2\,[M(OH)_2] + \ldots + [M_2OH] + 2[M_2(OH)_2] + \ldots . + p[M_m(OH)_p] + (p+1)[M_m(OH)_{p+1}] + \ldots . \qquad (12)$$

In the following way, however, it was possible to determine this point experimentally.

To the uranyl perchlorate was added an excess of perchloric acid. A base titration then indicated, that UO_2^{2+}, though acting as a rather strong acid, nevertheless was weak in comparison with $HClO_4$, and so the titration curve showed a well determinable point of inflection, indicating the point of equivalence (12), which thus was certainly found. The amount of base added to this point is equivalent with the amount of »free» acid present in the solution at the outset; this corresponds to an acid concentration C_H. This experimentally known quantity is the total $[H^+]$ at the outset, C_H^0, except that which might have been formed by an even in this solution possibly existing hydrolysis, $[H^+]_M$:

$$C_H = C_H^0 - [H^+]_M \qquad (13)$$

The »free» acid C_H, in its turn, combines from the extra perchloric acid added, 25.3 mC (30.1 mC at the glass electrode measurements)*, and the acid excess or deficit of the uranyl salt. The latter is proportional to the C_M at the start, C'_M. Thus we have

$$C_H = 25.3 + l \cdot C'_M \qquad (14)$$

where l ought to be a constant, if C_H is properly determined by the point of inflection. This proved to be the case, and so it was shown, that the points of equivalence searched for really coincide with the points of inflection found.

The hydrolytic reactions occur at $p[H^+]$ 2.5 to 5, so $[OH^-]$ of the solutions may always be quite neglected in comparison with the base amount added. The ligand number, defined according to (7), therefore in this system adopts the form $\bar{n} = C_{OH}/C_M$, where C_{OH} is the base taking part in UO_2^{2+} complex formation, that is the quantity used up by UO_2^{2+}. At a certain point of titration, this is

$$C_{OH} = B - (C_H^0 - [H^+]) + [H^+]_M \qquad (15\ a)$$

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* With this rather large acid addition, the solutions at the outset gave $p[H^+]$ 1.5—1.6. According to the extinctiometric measurements above, the hydrolysis of such solutions rather certainly is negligible. However this need not to be utilized in the present formulas or in the quinhydrone electrode measurements, but is confirmed there and will then be used in the glass electrode measurements.

where B = the total concentration of base added. — Introducing (13) we find

$$C_{\mathrm{OH}} = B - C_{\mathrm{H}} + [\mathrm{H}^+] \tag{15 b}$$

As C_{M} of a solution is always known from C'_{M}, corrected for the dilution, now we are finally able to calculate $\bar{n}$ from experimental data, according to

$$\bar{n} = \frac{C_{\mathrm{OH}}}{C_{\mathrm{M}}} = \frac{B - C_{\mathrm{H}} + [\mathrm{H}^+]}{C_{\mathrm{M}}} \tag{16}$$

It should be pointed out, that also the C_{H} originally determined has to be corrected for the dilution at the titration, when inserted in (15) and (16).

Now we plot $\bar{n}$ as a function of p[H$^+$] for the different C'_{M} used, and so we obtain the complex formation curves searched for.

The determinations have been extended over as wide a pH range as possible by continuing the titrations until a precipitate was definitively formed. This happened when $\bar{n}$ reached a value about 1.30.

Also the C'_{M} range was made as wide as possible, 2 to 60 mC (at the glass electrode 5 to 60 mC), to secure a good test of polynuclear complex formation. $C'_{\mathrm{M}} < 2$ would give too small a base consumption; $C'_{\mathrm{M}} > 60$ would certainly cause too large medium changes.

Measurements with the quinhydrone electrode

The electrode has once before been used in uranyl solutions by Singh and Ahmad [20].

The emf:s were measured with a Leeds-Northrup »Student's Potentiometer». The standard cell was a Weston cell of saturated type. As a zero instrument, a mirror galvanometer was used.

First, the behaviour of the electrode in uranyl solutions was controlled. It is true that any reduction of UO_2^{2+} by hydroquinone is not to be feared, as a calculation with the normal potentials shows, but on the other hand, one may imagine that a complex formation is possible between UO_2^{2+} and some quinhydrone component, preferably the hydroquinone.

This control had to be undertaken at so high a [H$^+$], that the hydrolysis could not disturb, not even in the solution richest in $[\mathrm{UO}_2^{2+}]$. I therefore chose pH $\approx$ 1, and prepared a cell

$$+\ \mathrm{Au} \left| \begin{array}{l} 100\ \mathrm{mC\ HClO_4} \\ 900\ \mathrm{mC\ NaClO_4} \\ \text{quinhydrone (s)} \end{array} \right\| \ \mathrm{RE} -$$

To the left half-cell a solution 200 mC $UO_2(ClO_4)_2$, 100 mC $HClO_4$, 300 mC $NaClO_4$ was added. Correction was introduced for the acid content of the uranyl salt, known from the main titrations (equ. (14)).

In this control, a deviation ΔE_q, increasing with C_M, was found between the observed and calculated emf:s:

Table 1. ΔE_q as a function of C_M

C_M mC	5	10	15	30	60	100
ΔE_q mV	0.1	0.2	0.3	0.7	1.4	2.6

The direction of ΔE_q was such that $[H^+]$ became higher than the proper value. This is just to be expected if a complex formation UO_2^{2+}-hydroquinone occurs. The effect cannot to any great extent be attributed to influences on the activity coefficient f_{H^+} by medium changes, as the analoguous control of the glass electrode (see below) gives a much smaller deviation. Nor is the effect to be ascribed to a salt error in the quinhydrone electrode. Such an error ought to appear in much the same degree at all divalent metal ions, but Leden [13, p. 93] has shown for Cd^{2+} and Fronaeus [12, p. 37] for Cu^{2+} that only a very small quinhydrone effect, if any, is to be found. A slight complex formation UO_2^{2+}-hydroquinone therefore seems to be the only reasonable explanation for the main part of ΔE_q.

ΔE_q causes an error in the measured $[H^+]$: s, the relative magnitude of which is determined by C_M or, rather, by $[UO_2^{2+}]$, as it may be assumed that the hydrolytic complexes show a very slight affinity for hydroquinone, having their places of co-ordination occupied by firmly bound OH^-:s. In the very beginning of the hydrolysis, $[UO_2^{2+}]$ is high and, moreover, $[H^+]$ is a considerable part of C_{OH}. So $\bar{n}$ is affected in a serious manner; at very small C_{OH} the calculation of $\bar{n}$ becomes quite illusory. As the hydrolysis proceeds, however, $[UO_2^{2+}]$ grows less and $[H^+]$ becomes smaller in comparison with C_{OH}: so the influence of ΔE_q rapidly decreases with increasing pH.

As a whole, however, the UO_2^{2+}-quinhydrone effect involves an uncertainity which among other things has lead to the control by the glass electrode.

By the hydrolysis titrations, cells of the following type are measured:

$$+\ \mathrm{RE}\ \left\| \begin{array}{l} [H^+] \\ C_M \\ \text{quinhydrone (s)} \\ I = 1\ (NaClO_4) \end{array} \right| \ \mathrm{Au}\ -$$

The emf in mV is given by

$$E_q = 58,2 \log \frac{10,10}{[H^+]} \qquad (17)$$

that is, if $-\log [H^+] = p[H^+]$ (18)

$$p[H^+] = \frac{E_q}{58.2} + 1,996 \qquad (19)$$

which gives $[H^+]$ * from the measured E_q, if we may neglect the hydroquinone complex formation, the effect of medium changes and the diffusion potentials.

The influence of hydroquinone complexes, and the medium effect and diffusion potential caused by UO_2^{2+} are included in the quinhydrone effect discussed above. Other medium changes occur through the diminishing of the ionic strength by the hydrolysis complex formation. By a separate experiment with lower ionic strength, it has been established, however, that the effect of this changes is to be neglected. The diffusion potentials depending on $[H^+]$, finally, may be estimated to ≈ 0.5 mV, at most, for those $[H^+]$ values which were used for $\bar{n}$-calculation; this error may also be neglected. So we find that (19) ought to be valid with great accuracy, if only $[H^+]$ is not too high (*i. e.* $\bar{n}$ too low). In the tables below, $\bar{n}$ is calculated only when the total systematic and experimental error is considered not to exceed ≈ 15 % of the value.

The potentials measured were very steady, and reproducible within ± 0.1 mV; they attained their proper value almost at once. No sign of any proceeding reaction in the solution could be detected. When precipitation occurs, the potential becomes disturbed and slips; this indicates the end-point of the titration.

The E_q measured at different C'_M are found in Table 2 A—F; according to (19) the $p[H^+]$ values have been calculated from these, and especially the $p[H^+]$ at the point of equivalence, $p[H^+]_{eq}$. This point is readily determined from E_q and the volume of base added, v_B, as the point of minimum buffer capacity. From v_{Beq} and v_H, the volume of the solution at the outset, C_H has been calculated, and so one is able to calculate C_{OH} and $\bar{n}$ according to (15 b) and (16). Then all quantities are known to form the complex formation function $\bar{n} = f\,(p[H^+])$, Fig. 2; and the function $\bar{n} \cdot [H^+] = f\,(1/[H^+])$, Fig. 3; used in the calculation of the constants.

From Fig. 2, it will at once be noted that $\bar{n} \approx 0$, when $p[H^+] < 2-2.5$, as predicted in the extinctiometric measurements.

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* Note, that the measurement gives $[H^+]$, not the activity a_H.

Table 2. Determination, by quinhydrone electrode, of $\bar{n}$ as a function of $p[H^+]$ and $\bar{n} \cdot [H^+]$ as a function of $1/[H^+]$, at different C_M.

*Table 2 A: $C'_M = 2.02$ mC ×**

$p[H^+]_{eq} = 3.71$
$v_{B_{eq}} = 5.00$ ml 94.8 mC + 1.85 ml 18.96 mC
$v_H = 20.0$ ml
$C_H = 25.5$ mC

v_B ml 18.96 mC **	E_q mV	(19) $p[H^+]$	$1/[H^+]$ mC^{-1}	(15 b) C_{OH} mC	C_M mC	(16) $\bar{n}$	$\bar{n} \cdot [H^+]$ $10^{-5} \cdot C$
	−22.1						
0	47.9	2.82					
1.40	78.0	3.34					
1.60	86.5	3.48					
1.80	96.0	3.65					
2.00	107.3	3.84	7.1	0.25	1.50	0.17	2.4
2.20	116.3	4.00	10.0	0.34	1.49	0.23	2.3
2.40	123.4	4.12	13.2	0.46	1.48	0.31	2.4
2.60	129.3	4.22	16.7	0.58	1.47	0.39	2.4
2.80	134.5	4.31	20.4	0.70	1.45	0.48	2.4
3.00	139.2	4.39	24	0.82	1.44	0.57	2.3
3.40	147.3	4.53	33	1.07	1.42	0.75	2.3
3.80	155.3	4.67	48	1.30	1.40	0.93	2.0
4.00	159.4	4.74	56	1.43	1.39	1.03	1.9
4.20	164.1	4.82	66	1.54	1.38	1.12	1.7
4.40	169.3	4.91	81	1.66	1.37	1.21	1.5
4.60	175.3	5.01	102	1.77	1.37	1.29	1.25
4.80	181.7	5.12	132	1.89	1.36	1.39	1.05

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* These signs are used to indicate the respective C'_M in the Figs 2, 3 and 4.

** First, 5.00 ml 94.8 mC NaOH is added to the starting solution (E_q = —22.1 mV); then the titration is continued with 18.96 mC NaOH (amounts in the first column).

Measurements with the glass electrode

The glass electrode, of the bulb type, was provided with a Ag-AgCl-electrode, dipping in 0.1 C HCl. It was manufactured by Radiometer, Copenhagen and used in connection with a Radiometer valve potentiometer. To avoid stray currents the stem of the electrode was covered with paraffine, and the measurements were made in a room of low moisture, arranged as an air thermostate.

To determine the slope *S*, the electrode was checked by three different kinds of buffer solutions, together covering the pH-range 1 to 6. They were prepared thus, that the pH-step between two solutions of the same kind had to be exactly one unit (*cf.* Fronaeus [12, p. 42]):

Table 2 B: $C'_M = 5.06$ *mC* ◆

$p[H^+]_{eq} = 3.40$
$v_{B_{eq}} = 5.44$ ml 94.8 mC
$v_H = 20.0$ ml
$C_H = 25.8$ mC

v_B ml 94.8 mC	E_q mV	(19) p[H$^+$]	[1/H$^+$] mC^{-1}	(15 b) C_{OH} mC	C_M mC	(16) $\bar{n}$	$\bar{n} \cdot [H^+]$ 10^{-5}· C
0	−22.5						
5.20	54.7	2.94					
5.30	63.6	3.09					
5.40	76.4	3.31					
5.50	90.0	3.54	3.5	0.51	3.97	0.13	3.7
5.60	101.4	3.74	5.5	0.77	3.95	0.195	3.5
5.70	109.2	3.87	7.4	1.10	3.93	0.28	3.8
5.80	115.2	3.99	9.8	1.42	3.92	0.36	3.7
5.90	121.2	4.08	12.0	1.77	3.90	0.455	3.8
6.00	126.2	4.17	14.7	2.11	3.89	0.54	3.7
6.10	130.7	4.24	17.2	2.46	3.87	0.635	3.7
6.20	135.1	4.32	20.8	2.80	3.86	0.73	3.5
6.30	139.2	4.39	24.5	3.14	3.84	0.82	3.4
6.40	142.3	4.44	28	3.49	3.83	0.91	3.3
6.50	147.4	4.53	33	3.82	3.81	1.00	3.0
6.60	151.8	4.60	40	4.16	3.80	1.09	2.7
6.70	156.7	4.69	49	4.50	3.79	1.19	2.4
6.80	162.3	4.79	62	4.84	3.78	1.28	2.1
6.90	168.8	4.90	79	5.16	3.77	1.37	1.7

Table 2 C: $C'_M = 10.11$ *mC* ●

$p[H^+]_{eq} = 3.17$
$v_{B_{eq}} = 5.52$ ml 94.8 mC
$v_H = 20.0$ ml
$C_H = 26.2$ mC

0	−23.3						
5.20	43.9	2.75					
5.30	50.2	2.86					
5.40	57.5	2.98					
5.50	66.3	3.14					
5.60	75.3	3.29	1.96	0.81	7.90	0.105	5.2
5.70	82.8	3.42	2.63	1.04	7.87	0.13	5.0
5.80	88.8	3.53	3.3	1.33	7.84	0.17	5.1
6.00	98.8	3.70	5.0	1.95	7.78	0.25	5.0
6.20	105.6	3.81	6.4	2.61	7.72	0.34	5.3
6.40	111.4	3.91	8.1	3.28	7.66	0.43	5.3
6.60	116.6	4.00	10.0	3.95	7.61	0.52	5.2
6.80	121.1	4.08	12.0	4.61	7.56	0.61	5.1
7.20	130.8	4.24	17.2	5.91	7.44	0.79	4.6
7.60	140.1	4.40	25.0	7.19	7.33	0.98	3.9
8.00	149.1	4.56	36	8.43	7.22	1.16	3.2

Table 2 D: $C'_M = 15.17$ *mC* ▲

$p[H^+]_{eq} = 3.02$
$v_{B_{eq}} = 5.65$ ml 94.8 mC
$v_H = 20.0$ ml
$C_H = 26.8$ mC

v_B ml 94.8 mC	E_q mV	(19) $p[H^+]$	$1/[H^+]$ mC^{-1}	(15 b) C_{OH} mC	C_M mC	(16) $\bar{n}$	$\bar{n} \cdot [H^+]$ $10^{-5} \cdot C$
0	−24.1						
5.50	49.5	2.85					
5.60	55.9	2.96					
5.70	62.7	3.08					
5.80	69.3	3.19	1.54	1.20	11.8	0.10	6.6
5.90	75.1	3.29	1.96	1.43	11.7	0.12	6.3
6.00	79.5	3.36	2.27	1.72	11.7	0.145	6.4
6.50	96.0	3.64	4.4	3.27	11.4	0.285	6.6
7.00	106.5	3.83	6.8	4.89	11.2	0.435	6.5
7.40	113.6	3.95	8.9	6.16	11.1	0.555	6.2
7.80	120.1	4.06	11.5	7.41	10.9	0.68	5.9
8.20	126.1	4.16	14.5	8.64	10.8	0.80	5.5
8.60	132.1	4.26	18.2	9.84	10.6	0.93	5.1
9.00	138.2	4.37	23.2	11.0	10.5	1.05	4.5
9.40	144.7	4.48	30	12.1	10.3	1.17	3.9
9.80	152.1	4.60	40	13.2	10.2	1.30	3.2

Table 2 E: $C'_M = 30.34$ *mC* ▼

$p[H^+]_{eq} = 2.83$
$v_{B_{eq}} = 6.00$ ml 94.8 mC
$v_H = 20.0$ ml
$C_H = 28.4$ mC

0	−26.0						
5.70	36.1	2.62					
5.80	40.0	2.69					
5.90	44.0	2.76					
6.00	48.4	2.83					
6.10	52.6	2.90					
6.20	56.7	2.97	0.93	1.79	23.2	0.077	8.2
6.50	67.0	3.15	1.41	2.50	22.9	0.11	7.8
7.00	78.5	3.35	2.22	3.96	22.5	0.175	7.9
7.60	88.1	3.51	3.2	5.81	22.0	0.265	8.2
8.40	97.5	3.67	4.7	8.22	21.4	0.385	8.2
9.20	105.2	3.80	6.3	10.6	20.8	0.51	8.1
10.00	112.1	3.92	8.3	12.8	20.2	0.635	7.6
10.80	118.6	4.03	10.6	14.9	19.7	0.755	7.1
11.60	124.7	4.14	13.7	16.9	19.2	0.88	6.4
12.10	128.6	4.20	15.9	18.1	18.9	0.96	6.0
12.60	132.5	4.27	18.5	19.3	18.6	1.04	5.6
13.10	136.1	4.33	21.3	20.4	18.4	1.11	5.2
13.60	139.8	4.40	25	21.4	18.2	1.18	4.7

Table 2 F: $C'_M = 60.7$ *mC*

$p[H^+]_{eq} = 2.63$
$v_{B_{eq}} = 3.40$ ml 94.8 mC
$v_H = 10.0$ ml
$C_H = 32.2$ mC

v_B ml 94.8 mC	E_q mV	(19) p[H+]	1/[H+] mC^{-1}	(15 b) C_{OH} mC	C_M mC	(16) $\bar{n}$	$\bar{n} \cdot [H^+]$ $10^{-5} \cdot C$
0	−29.9						
3.20	26.4	2.45					
3.30	31.4	2.54					
3.40	36.9	2.63					
3.50	42.3	2.72					
3.60	47.4	2.81	0.64	2.94	44.6	0.066	10.2
3.70	51.8	2.89	0.77	3.38	44.3	0.076	9.9
3.80	55.6	2.95	0.89	3.87	44.0	0.088	9.9
4.00	61.8	3.06	1.15	4.94	43.4	0.115	9.9
4.20	66.9	3.15	1.41	6.05	42.8	0.14	10.0
4.60	74.5	3.28	1.92	8.30	41.6	0.20	10.4
5.00	80.5	3.38	2.38	10.5	40.5	0.26	10.9
5.40	85.5	3.47	2.94	12.6	39.4	0.32	10.9
5.80	90.3	3.55	3.6	14.7	38.4	0.38	10.6
6.20	94.5	3.62	4.2	16.6	37.5	0.445	10.6
6.60	98.7	3.69	4.9	18.5	36.6	0.505	10.3
7.00	102.3	3.76	5.8	20.3	35.7	0.57	9.9
7.40	106.0	3.82	6.6	22.0	34.9	0.63	9.5
8.20	112.8	3.94	8.7	25.1	33.4	0.75	8.6
9.00	119.6	4.06	11.5	28.0	32.0	0.875	7.6
9.80	126.4	4.18	15.1	30.7	30.6	1.00	6.6
10.60	133.4	4.29	19.6	33.2	29.5	1.13	5.8
11.40	140.8	4.42	26.3	35.5	28.4	1.25	4.8
12.20	148.3	4.54	34.5	37.6	27.4	1.37	4.0

1. 100 mC $HClO_4$ / 900 mC $NaClO_4$ and 10 mC $HClO_4$ / 990 mC $NaClO_4$ for the step 1 → 2;
2. 1000 mC NaClAc * / 500 mC HClAc, 1000 mC NaClAc / 50 mC HClAc and 1000 mC NaClAc / 5 mC HClAc

   for the steps 3 → 4 and 4 → 5;
3. 1000 mC NaAc ** / 500 mC H Ac and 1000 mC Na Ac / 50 mC H Ac for the step 5 → 6.

At pH 1 → 2, [H+] is so high that one must take the diffusion potential into consideration. It has been measured by quinhydrone electrode to reach

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* $ClAc^-$ = chloroacetate ion.

** Ac^- = acetate ion.

5.5 mV *. At the higher pH:s, the diffusion potentials are negligible. — With this correction, a constant value $S = 57.5 \pm 0.5$ mV is found over the whole pH-range and used in the following calculations.

The behaviour of the electrode in UO_2^{2+}-solutions was then controlled in a manner analogous to the quinhydrone electrode, Tab. 3:

Table 3. ΔE_g as a function of C_M

C_M mC	5	10	15	30	60	100
ΔE_q mV	0.1	0.1	0	0.2	0.3	0.8

The deviations found, ΔE_g, were very slight even at high C_M. They are to be considered as pure effects of medium change. So the glass electrode ought to give $[H^+]$ free from such systematic errors as ΔE_q causes at the quinhydrone electrode.

By the hydrolysis titrations, cells of the following type were measured:

$$+ \text{ RE} \left\| \begin{array}{l} H^+] \\ C_M \\ I = 1 \ (NaClO_4) \end{array} \right| \begin{array}{l} \text{glass} \\ \text{electrode} \ - \end{array}$$

The direct measured emf E_g in mV is given by

$$E_g = E_{RE} - E_{AgCl} - S \log \frac{a_{H^+}}{a_{HCl}} - A \qquad (20)$$

where

E_{RE} and E_{AgCl} are the potential jumps of the RE and Ag, AgCl-electrode; a_{H^+} and a_{HCl} the hydrogen ion activities of the measuring solution and of 0.1 C HCl; A is the asymmetry potential of the glass electrode.

E_{RE}, E_{AgCl} and $S \log a_{HCl}$ are constants, their sum is a constant E_k. Hence

$$E_g = E_k - A - S \log a_{H^+} \qquad (21\text{ a})$$

Only over a short period of time A is a constant; by measuring a standard solution of known $[H^+] = [H^+]_0$ on the same occasion we may, however, write:

$$E_g^0 = E_k - A - S \log a_{H_0^+} \qquad (21\text{ b})$$

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* The formula of Henderson gives 5.3 mV.

Further, as the same ionic medium is used in both cases, $a_{H^+}/a_{H^+_0} = [H^+]/[H^+]_0$ and so we obtain

$$E_g - E_g^0 = S \cdot \log \frac{[H^+]_0}{[H^+]} \tag{22 a}$$

Table 4. Determination, by glass electrode, of $\bar{n}$ as a function of p [H+] and $\bar{n} \cdot$ [H+] as a function of 1/[H+], at different C_M.

Table 4 A: C'_M = 5.03 mC ◆

$p[H^+]_{eq} = 3.41$
$v_{B_{eq}} = 5.87$ ml 100.9 mC
$v_H = 20.0$ ml
$C_H = 29{,}6$ mC and $E_g^{(10)} - E_g^{(C_H)} = 26.4$ mV

v_B ml 100.9 mC	$E_g - E_g^{(10)}$ mV	(23) $p[H^+]$	$1/[H^+]$ mC^{-1}	(15 b) C_{OH} mC	C_M mC	(16) $\bar{n}$	$\bar{n} \cdot [H^+]$ $10^{-5} \cdot C$
0	−26.4						
5.60	53.3	2.93					
5.70	61.5	3.07					
5.80	72.2	3.25					
5.90	84.9	3.48	3.0	0.45	3.89	0.115	3.8
6.00	96.5	3.68	4.8	0.72	3.87	0.185	3.9
6.20	112.2	3.95	8.9	1.38	3.84	0.36	4.0
6.40	123.2	4.14	13.7	2.09	3.81	0.55	4.0
6.60	132.1	4.30	20.0	2.82	3.78	0.745	3.8
6.80	140.4	4.44	28	3.54	3.75	0.945	3.4
7.00	148.7	4.59	39	4.25	3.73	1.14	2.9
7.20	158.2	4.75	56	4.96	3.70	1.34	2.4

Table 4 B: C'_M = 15.08 mC △

$p[H^+]_{eq} = 3.07$
$v_{B_{eq}} = 4.33$ ml 100.9 mC
$v_H = 15.0$ ml
$C_H = 29.1$ mC and $E_g^{(10)} - E_g^{(C_H)} = 26.0$ mV

0	−26.0						
4.10	42.1	2.73					
4.20	49.6	2.86					
4.30	58.6	3.02					
4.40	68.4	3.19	1.54	1.01	11.7	0.087	5.7
4.50	76.1	3.32	2.08	1.36	11.6	0.115	5.6
4.60	82.4	3.43	2.7	1.76	11.5	0.155	5.6
4.80	91.8	3.60	4.0	2.65	11.4	0.23	5.7
5.20	104.8	3.82	6.6	4.50	11.2	0.395	6.0
5.60	114.6	3.99	9.8	6.33	11.0	0.575	5.9
6.00	123.0	4.14	13.9	8.10	10.8	0.75	5.4
6.40	131.2	4.28	18.9	9.82	10.55	0.93	4.9
6.80	139.3	4.42	26	11.5	10.4	1.11	4.2
7.20	148.1	4.57	37	13.1	10.2	1.29	3.5

Table 4 C: $C'_M = 60.1$ *mC* □

$p[H^+]_{eq}$ = 2.66
$v_{B_{eq}}$ = 2.73 ml 100.9 mC
v_H = 10.0 ml
C_H = 27.5 mC and $E_g^{(10)} - E_g^{(C_H)}$ = 24.6 mV

v_B ml 100.9 mC	$E_g - E_g^{(10)}$ mV	(23) $p[H^+]$	$1/[H^+]$ mC^{-1}	(15 b) C_{OH} mC	C_M mC	(16) $\bar{n}$	$\bar{n} \cdot [H^+]$ $10^{-5} \cdot C$
0	−24.6						
2.50	25.4	2.44					
2.60	30.6	2.53					
2.70	36.3	2.63					
2.80	42.1	2.73					
2.90	47.4	2.82	0.66	2.8	46.6	0.060	9.1
3.00	52.3	2.91	0.81	3.3	46.2	0.071	8.7
3.40	65.8	3.15	1.41	5.7	44.8	0.125	9.0
4.00	78.5	3.37	2.32	9.6	42.8	0.225	9.7
4.60	86.6	3.51	3.2	13.2	41.2	0.32	9.9
5.40	96.0	3.67	4.7	17.7	39.0	0.455	9.7
6.20	104.2	3.81	6.5	21.8	37.1	0.59	9.1
7.00	111.8	3.94	8.7	25.5	35.3	0.72	8.3
8.00	120.6	4.10	12.5	29.6	33.3	0.89	7.1
9.00	129.3	4.25	17.8	33.4	31.6	1.06	5.9
10.00	138.2	4.40	25	36.7	30.0	1.22	4.9

from which $[H^+]$, the only unknown quantity, may be calculated. The assumption made, that A is a constant during the time of a titration series gives as a consequence that E_g—E_g^0 at a certain point ought to be a constant if the titration is repeated. This proves to be the case, and so the assumption must be true.

As a solution of known $[H^+]$ to be measured at the same occasion as the unknown $[H^+]$, it is suitable to choose the solution before titration. As stated above, the hydrolysis of a solution of such a high acidity as 30 mC may be neglected. $\therefore$ $[H^+]_M = 0$, $C_H^0 = C_H = [H^+]_0$ (13), where C_H is experimentally determined.

On the other hand, a considerable diffusion potential arises at this high acidity, as it has been stated at the determination of S above. This must be corrected for, if the determined constant value $S = 57.5$ is to be used. To avoid this correction, the solution with $[H^+] = 10$ mC was choosen as a standard instead of the solution at the outset; for from $p[H^+]$ 2 upwards the diffusion potentials might be neglected. Moreover, this $p[H^+]$ was the standard of the quinhydrone electrode measurements * (see (17)), which thus become directly comparable with those of the glass electrode.

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* Or, exactly, $p[H^+] = 1.996$.

But for the use of $[H^+] = 10$ mC as a standard solution, it was necessary to know its E_g difference to the directly measured solution at the outset. This was determined by base titrations without UO_2^{2+} : it was found that the difference in E_g between $[H^+] = 30.1$ mC and $[H^+] = 8.2$ mC is 31.6 mV; hence the apparent slope without diffusion potential correction was 56.0 in this range. With this figure, the E_g difference between the C_H of the measuring series and $[H^+] = 10$ mC was calculated (Table 4).

With the choosen $[H^+]_0 = 10.0$ mC and $S = 57.5$, (22 a) becomes

$$E_g - E_g^{(10)} = 57.5 \log \frac{10.0}{[H^+]} \qquad (22\ b)$$

and hence

$$p[H^+] = \frac{E_g - E_g^{(10)}}{57.5} + 2.00 \qquad (23)$$

The reproducibility of E_g increases with the buffering capacity of the solution; at low C_M in the proximity of the point of equivalence it was as poor as ± 0.5 mV, but in most cases one may calculate to ± 0.2 mV.

E_g attained as a rule its final value within a few minutes; at low $p[H^+]$ or when a great $p[H^+]$ jump had just occurred, a longer time was needed. The attained values were steady.

As a whole, the accidental errors were severely larger than for the quinhydrone electrode; on the other hand the systematic errors were considerable smaller, as was stated above. Here too, $\bar{n}$ was not calculated from the measured potentials, if the error might exceed $\approx 15\ \%$.

The measurements are given in Tables 4 A—C and in Figs. 2 and 3 the curves $\bar{n} = f\ (p[H^+])$ and $\bar{n} \cdot [H^+] = f\ (1/[H^+])$ are found.

Conclusions from the measurements

As seen from Figs. 2 and 3, both the $[H^+]$ measuring methods used give essentially the same result. The deviations between the curves when C'_M is 60 mC and 15 mC are to be expected on account of the UO_2^{2+}-hydroquinone complex formation, and the deviation at $C'_M = 5$ mC is most likely to be explained by the accidental error, which is large at low C_M especially for the glass electrode.

The $\bar{n} = f\ (p[H^+])$ curves do not coincide, not even for the lowest C'_M. So the hydrolysis reaction involves a polynuclear complex formation, and so strongly pronounced that it manifests itself very distinctly even at so low a

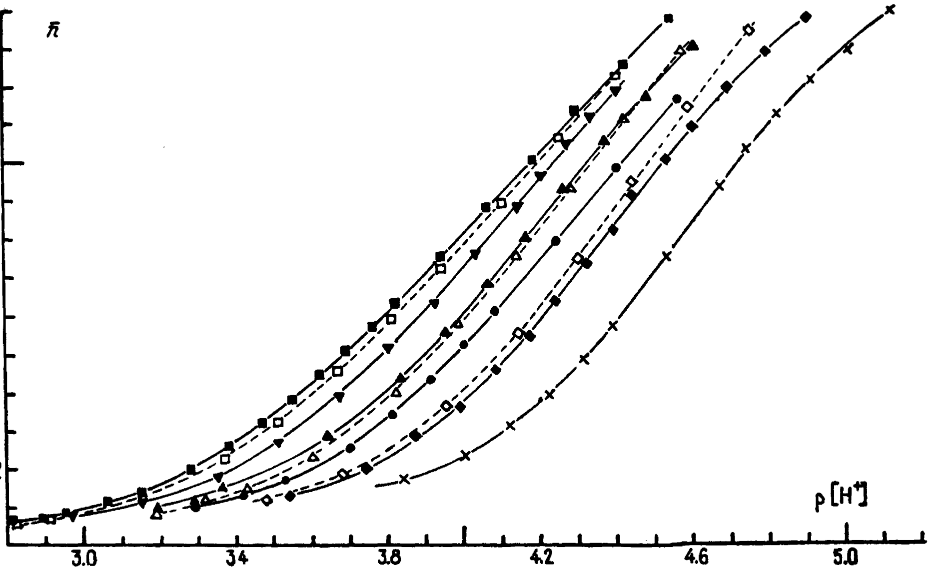

Fig. 2. Complex formation curves of the hydrolysed uranyl system at different C'_M, indicating the existence of polynuclear complexes. — The different signs relate to C'_M-values according to Tables 2 and 4. Filled signs and fulldrawn curves relate to the quinhydrone electrode measurements; open signs and dashed curves to the glass electrode measurements.

C_M as $\approx$ 5 mC. As it has been proved above, it is quite impossible that diffusion potentials, medium changes or electrode effects are the causes of the deviations.

This tendency of polynuclear complex formation puts the conditions in the uranyl solutions in a striking analogy to those existing in chromate, molybdate, and tungstate solutions (see *e. g.* Jander and Jahr [21]). Thus all metals of the group VI a in their six-valent state appear as complex ions, containing oxygen. These are in the cases CrO_4^{2-}, MoO_4^{2-} and WO_4^{2-} bases (in the sense of Brønsted) with increasing strength in the order mentioned, while UO_2^{2+} is an acid. When the ionic charge is forced to diminish, which happens by increasing [H^+] at the ions of Cr, Mo, and W, but at decreasing [H^+] at the U-ion, then all these metal-oxygen ions show a very strong tendency to aggregate, a tendency which before was compensated by strong Coulomb forces *.

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* Curiously enough, Jander and Jahr [22] have come to the result, that the aggregation they have proved in solutions of chromate, molybdate, and tungstate would not occur in uranyl solutions. The reverse is to be expected, and the present results proves that this is the case.

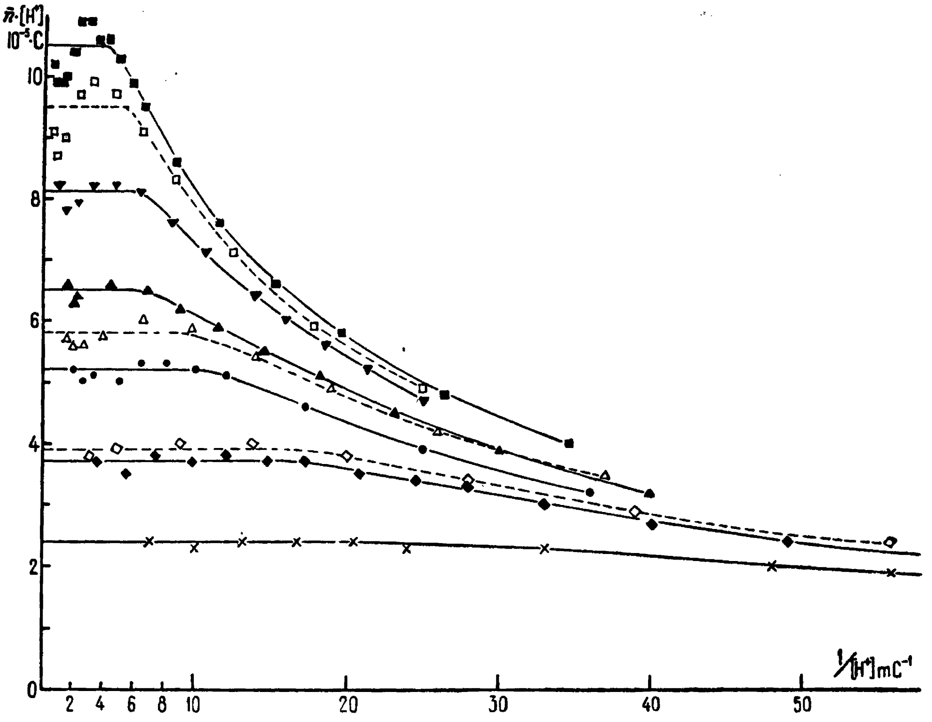

Fig. 3. $\bar{n}\cdot[H^+]$ *as a function of* $1/[H^+]$, *to determine* $\lim \bar{n}\cdot[H^+]$, *when* $1/[H^+] \to 0$. — *About the signs, see Fig. 2.*

By other hydrolysis reactions, too, polynuclear complexes exist. This has been proved qualitatively for numerous metal ions (especially by Jander and Jahr[22]) and, more recently, also quantitatively for Bi^{3+} (Granér and Sillén[23]) and for Cu^{2+} (Pedersen[24]). So a polynuclear complex formation in such reactions seems to be a rule rather than an exception.

For the calculation of the constants $\varkappa_1'$ and $\varkappa_1''$, the limits $\bar{n}\,[H^+]$ when $1/[H^+] \to 0$ were extrapolated from Fig. 3. The limits found are in Table 5, together with the values of C_M at the lowest determined $\bar{n}$ (at these C_M the extrapolations of Fig. 3 are made, and so they are to be inserted in (11)). In Fig. 4, finally, the limits are plotted as a function of C_M. As predicted, the found curve is with good approximation a straight line in its first part. From its axis interception and slope we get, (11):

$$\varkappa_1' = (2.0 \pm 0.4)\cdot 10^{-5}\ C; \qquad \varkappa_1'' = (4 \pm 1)\cdot 10^{-3}$$

Table 5. *lim* $\bar{n}$. $[H^+]$ *as a function of* C_M. $1/[H^+] \rightarrow 0$

C'_M mC	quinhydrone		glass	
	lim $\bar{n}$ · $[H^+]$ 10^{-5} · C	C_M mC	lim $\bar{n}$ · $[H^+]$ 10^{-5} . C	C_M mC
2	2.4	1.5	—	—
5	3.7	4.0	3.9	3.9
10	5.2	7.9	—	—
15	6.4	11.8	5.8	11.7
30	8.1	23	—	—
60	10.5	45	9.5	47

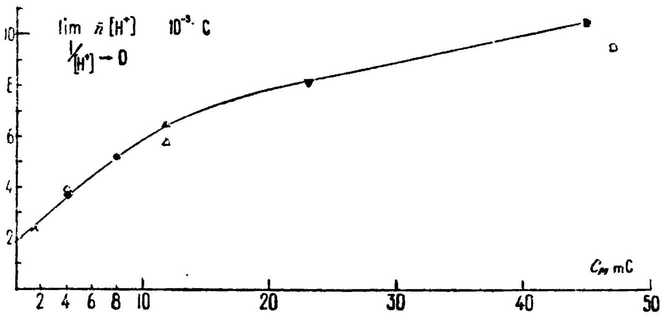

Fig. 4. Lim $\bar{n}$ · $[H^+]$ *as a function of* C_M*, to determine* $\varkappa'_1$ *and* $\varkappa''_1$ · $1/[H^+] \rightarrow 0$. — *About the signs, see Fig. 2. — The curve is drawn in accordance with the points of the quinhydrone electrode measurements.*

If we assume $K_W = 10^{-14}$, this corresponds to β values, (9) : $\beta'_1 = 2 \cdot 10^9$ C^{-1}; $\beta''_1 = 4 \cdot 10^{11}$ C^{-2}.

At higher C_M, the curve, according to (11) ought to bend upwards, if it bends at all. Unfortunately, the contrary is the case. The only reasonable explanation of this seems to be that the limits searched for are not attained at higher C_M, and, further, the curves here have such a course that the extrapolation gives an entirely misleading result. That the proper limits really are attained at low C_M is just proved by the fact that (11) in these cases really has the predicted course.

SUMMARY

It has been shown by extinctiometric measurements that the uranyl ion UO_2^{2+} is the only existing complex of six-valent uranium in aqueous solution from $p[H^+] \approx 0.1$ (the lowest investigated) up to $p[H^+] \approx 2$. Over that

p[H$^+$] further hydrolysis complexes are gradually formed. So UO_2^{2+} may be regarded as a complex forming central group, and formulas for its complex formation have been developed in a manner analogous to other metal ions.

The extinction curve of UO_2^{2+} has been determined; by this the data of the literature have been found to be erroneous.

As the first complex uranyl system to be investigated, just the further hydrolysis of UO_2^{2+} has been selected. It has been studied by [H$^+$] measurements when $UO_2(ClO_4)_2$ solutions were titrated with NaOH. The total uranium concentration ranged from 2 mC to 60 mC. The ionic strength of the solutions was kept constant = 1 by the aid of $NaClO_4$.

The determinations were done, firstly with quinhydrone electrode, secondly with glass electrode. Both electrodes gave essentially the same image of the hydrolysis complex formation, which thus with certainity may be described as follows:

The hydrolysis becomes appreciable at p[H$^+$] $\approx$ 3. Precipitation does not occur until, on the average, 1.3 OH^- has been used per UO_2^{2+}; p[H$^+$] is then 4.5-5.

The complex formation curves found at different C_M prove without any doubt that a polynuclear complex formation plays a very important role in the hydrolysis, even at the smallest C_M. This fact places UO_2^{2+} in an analogous position to other metallic ions, containing oxygen, in the same group of the periodic system: CrO_4^{2-}, MO_4^{2-}, WO_4^{2-}.

The first mononuclear dissociation constant $\varkappa_1$ and the first dinuclear $\varkappa_1''$, defined above, have been determined. At 20° C they were found to be, for the ionic medium used,

$$\varkappa_1' = (2.0 \pm 0.4) \cdot 10^{-5}\ C; \qquad \varkappa_1'' = (4 \pm 1) \cdot 10^{-3}$$

These uranyl investigations have been suggested to me by my teacher in chemistry, Professor Sven Bodforss, to whom I am very much indebted for the valuable aid he has given in different respects.

With my friend Docent Sture Fronaeus I have had many fruitful discussions. They have given me views and information, which have strongly promoted my work.

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