

Studies on the Hydrolysis of Metal Ions

46. Uranyl Ion, UO_2^{2+} , in Chloride, Perchlorate, Nitrate, and Sulfate Media. Survey and Introduction

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A survey is given of emf work, started at KTH ** in 1956, on the hydrolysis of the UO_2^{2+} ion in the media 3 M (Na)Cl, 3 M (Mg)ClO₄, 3 M (Ca)ClO₄, 3 M (Na)ClO₄, 1 M (K)NO₃, 1.5 M (Na)SO₄. Detailed data and calculations will be given in separate papers; the publication has been delayed for external reasons. Thanks to the MESAK and LETAGROP computer programs, equilibrium analysis data can be presented in a more concise way than previously. Figs. 1 a-1 f are MESAK diagrams of the average composition (\bar{p}, \bar{q}) of the complexes $(\text{UO}_2)_q(\text{OH})_p$; they bear out the differences between the reactions in the various media.

Table 1 gives a survey of the "best" sets of the species and equilibrium constants obtained by LETAGROP refinement.

Equilibrium analysis leaves little doubt about the existence of the species (1,2), (2,2), (4,3) and (5,3), though their relative importance varies with the medium. The existence also of some higher members of the series (2 n , $n + 1$) is indicated, especially in sulfate medium. There is some evidence for the (1,1) complex though its formation constant is much smaller than given by early authors. In NaCl medium another species, probably (7,4) is indicated.

Complexing with the medium anion is discussed, obvious effects being the chloride complexing of the (4,3) complex, and the strong sulfate complexing of all species.

NOTATION

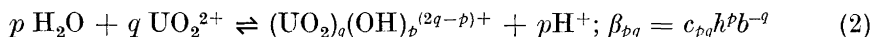
In analogy with other papers in this series the hydrolysis of the uranyl ion will be treated as reactions between the reagents $A = (-\text{H}^+)$ and $B = \text{UO}_2^{2+}$. In the general equations of equilibrium analysis the free concentrations of the reagents are then

$$a = [\text{H}^+]^{-1} = h^{-1}; \quad b = [\text{UO}_2^{2+}] \quad (1)$$

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We let β_{pq} be the equilibrium constant for the reaction:



where c_{pq} stands for the concentration of the complex. For the sake of consistency we are going to refer to the complex in eqn. (2) as the (p, q) complex, thus giving the OH number first. The formulas will be written uniformly with OH as ligand; the species may however contain O-bridges instead of $(\text{OH})_2$ -bridges, and water of hydration.

The total (analytical) concentrations of uranyl and hydrogen ions are denoted by B and H ; in hydrolysed solutions, H is usually negative. If Z is the average number of OH^- bound, or H^+ set free, per UO_2^{2+} , we have the relationships

$$B = b + \sum q c_{pq} = b + \sum q \beta_{pq} h^{-p} b^q \quad (3)$$

$$BZ = \sum p c_{pq} = \sum p \beta_{pq} h^{-p} b^q = h - H \quad (4)$$

EARLIER WORK

The hydrolysis of the uranyl ion, UO_2^{2+} , has been studied repeatedly. For an almost complete list of earlier work the reader is referred to the IUPAC "Tables of stability constants",¹ the second edition of which lists about 30 papers on the subject. The first author quoted there (Heidt 1942) presumes, as was then customary, that the main product is the mononuclear ion UO_2OH^+ . However, any attempt to measure at several UO_2^{2+} concentrations reveals that the main products must be polynuclear, and already in 1947 several authors (McInnes, Guiter, Schaal and Faucherre) claimed evidence for the (2,2) complex.

Sten Ahrland² in 1949 made what was till then the most extensive measurements of UO_2^{2+} hydrolysis over a considerable range of the total uranyl concentration, B , and $\log h$. Obviously, the shape of the curves at higher Z could not be explained by the (2,2) complex alone. In a recalculation of Ahrland's data (1954), Ahrland, Hietanen and Sillén³ observed that the data, plotted as $Z(\log h)_B$, are on practically parallel curves, which would indicate the general composition $(2n, n+1)$ of the complexes. Since the accuracy of the available data did not seem to make a more detailed treatment advisable, and the deviations were considered by the first author to be within his possible experimental errors, the explanation of an unlimited series of complexes $(2n, n+1)$ was given. For this description only two equilibrium constants were needed.

Survey of work on uranyl hydrolysis at KTH from 1956

In the following years, the group at KTH in Stockholm carried out an extensive study of the hydrolysis of various metal ions with gradually improving experimental and computation methods. It was thought desirable to study also whether the hydrolysis reactions vary with the ionic medium, and so, studies of the hydrolysis of UO_2^{2+} in sulfate and chloride media were started in 1956.

The sulfate studies, by Alf Peterson ⁴ (starting April 1956) seemed on the whole to agree with the earlier picture. The data were considerably more accurate than the earlier perchlorate data, and were found to fall (within the limits of error) on parallel curves, except for small deviations at the very lowest total concentrations B , which were ascribed to an impurity. This work therefore seemed to confirm the $(2n, n+1)$ formula. To explain the data well, Peterson had to assume at least the first four members: (2,2), (4,3), (6,4) and (8,5).

The nitrate work, which was started by Helen Dunsmore in September 1956, indicated some deviations from parallelity. It was thought at first that they might be due to experimental errors, but increasing the accuracy only confirmed the deviations, which were too large to allow calculation even of the (2,2) and (4,3) complex constants by the methods then available — mainly comparison with projection maps, calculated by means of desk calculating machines. In September 1957, attention was turned to chloride medium and the deviations in this medium were found to be smaller than in nitrate which permitted the calculation of approximate constants for the (2,2), (4,3), and (6,4) complexes and the deviations to be ascribed to the existence of the (5,3) complex and possibly also the (7,4) complex. These results were obtained already in the summer of 1958.

In the light of these results, it became very desirable to reinvestigate the hydrolysis of UO_2^{2+} in perchlorate medium, using the improved techniques that had been worked out at KTH in the meantime. In 1958 Sirkka Hietanen ⁵ had studied the hydrolysis of UO_2^{2+} in "self-medium", 1.4 M UO_2^{2+} , 3 M (Na)ClO₄, and found evidence for the (1,2) complex, $(\text{UO}_2)_2\text{OH}^{3+}$. Beginning in June 1959 she carried out a study of UO_2^{2+} hydrolysis in 3 M (Na)ClO₄ medium at 25°C. These studies were also prompted by the fact that Kurt Schlyter needed the equilibrium data for evaluating his enthalpy titrations of the uranyl hydrolysis reactions in this medium.

Sirkka Hietanen's data revealed a much larger deviation from parallelity than had been obtained with the chloride medium, and again strongly indicated the (5,3) complex. In early 1960, she gave the following preliminary constants $\log \beta_{22} = -6.03$, $\log \beta_{43} = -13.20$, $\log \beta_{53} = -16.55$, $\log \beta_{64} = -19.42$ which were then used in Kurt Schlyter's work.⁶

In 1960, Sirkka Hietanen carried out studies on uranyl hydrolysis in 3 M (Mg)ClO₄ medium, and in the beginning of 1961, together with B.R.L. Row, in 3 M (Ca)ClO₄ medium. In the meantime, Helen Dunsmore, who had gone to Glasgow in the autumn of 1959, worked with nitrate medium to extend the range of data available.

Improvements in methods of equilibrium analysis

Our work on uranyl hydrolysis, which has been extended in time, has coincided with a rapid development of our methods for computation.

When the work began, we were restricted to desk computers, but in the meantime we worked out a series of programs for electronic computers. By the integration method (Sillén ⁷) and our computer program MESAK (to be

described elsewhere), a diagram of the average composition of the complexes (\bar{p}, \bar{q}) can be calculated directly from the data, without any assumption except that the law of mass action holds and that the data are correct. The MESAK program also makes it possible to subtract one or more complexes, assuming various values for their formation constants, and calculate the average composition of the remaining complexes.

The MESAK diagram or diagrams indicate the sets of complexes that ought to be considered. Using our generalized least squares program LETAGROP or its more recent improved version LETAGROPVRID, we may then find the "best" set of constants for each set of complexes. The LETAGROP family of programs is very versatile, and can be used for refining constants sought, from any kind of weighted or unweighted data.^{8,9}

In spite of every precaution, the choice between various conceivable sets of complexes may be marred by small systematic errors; however, if a good set of data is available one can usually make what seems to be a reliable conclusion as to what the main complexes are. The guiding principles are that the standard deviation in Z (or whatever quantity is considered as carrying the error) should be minimized, that there should be as few systematic deviations as possible between calculated and observed values, and that explanations with fewer variable parameters are preferred if everything else is comparable. There are certainly borderline cases but the main species will seldom be in doubt.

We are not saying that the final results — species and equilibrium constants — differ very much from those that would be obtained by using the old methods with desk computers, but the new computer methods have saved much time which can now be used for chemical work. They make it possible to carry the refinement a little further, to test more hypotheses and to express in a more concise way why certain hypotheses are rejected.

It may be mentioned that in August 1961 one of us (LGS) showed in the USA a few slides where the hydrolysis of UO_2^{2+} , and the refinement of β_{22} , β_{42} , β_{53} and β_{64} was used as an example of how LETAGROP works (Gordon conference on inorganic chemistry, August 21, 1961; and 6ICCC on August 29, 1961 at Detroit). He was then unaware of the fact that by that time workers at Oak Ridge (Rush *et al.*) had independently decided on the (5,3) complex.

From 1962 on, these workers started publishing their studies on uranyl hydrolysis.¹⁰⁻¹² They have been working with an ultracentrifuge, with spectral methods, and with emf methods; out of which the emf data, as usual, give the most precise answers.

It is deplorable that the publication of our work has been delayed by an excess of other urgent work, both in Stockholm and in Glasgow.

In the argument of this and following papers on uranyl hydrolysis, we shall only use the emf data that we have obtained in Stockholm and Glasgow, since we are of the opinion that emf data can and should be used as far as possible as a basis for deducing the predominant equilibria without recourse to information obtained by other methods. When that is done, comparison can begin.

NOTES ON THE PRESENTATION OF EQUILIBRIUM ANALYSES

Thanks to the MESAK and LETAGROP programs, papers on equilibrium analysis can in the future be written in a more concise way than previously, as will be exemplified by the following papers. (A parallel might be drawn with the new look of papers on crystal structure analysis, after the advent of the Patterson, Fourier and least-square computer methods).

The following arrangement may, for instance, prove practical for a complicated system.

- 1) Problem, previous work.
- 2) Experimental details: purity, analyses, equilibrium attainment.
- 3) Data in full in some form such as $Z(\log a)_B$, which is easily plotted or fed to a computer, whenever a recalculation proves desirable.
- 4) MESAK diagram (\bar{p}, \bar{q}) possibly also some "subtracted" MESAK diagrams.
- 5) LETAGROP treatment: which sets of species were tried, "best" values for β_{pq} with standard deviations $\sigma(\log \beta_{pq})$, and $\sigma(Z)$, for the combination finally preferred, and also for one or two of the "best" combinations of those that were rejected.
- 6) Comparison of experimental and calculated values. Since the deviations are in general too small to be seen very well on a printed diagram, the following system has been adopted in the papers to follow. An experimental point which falls within the limits $Z_{\text{calc}} \pm 0.5\sigma(Z)$ is given as an empty circle. If the deviations are between $0.5\sigma(Z)$ and $1.5\sigma(Z)$, a circle with a *thin* plus or minus sign is given. The sign shows in which direction the *calculated* Z -value deviates from the experimental one; *a priori*, we believe more in the experiments. If the deviations are larger than $1.5\sigma(Z)$, *thick* plus or minus signs are given. In this way it is easy to see whether the spread is reasonably random or whether there are systematic deviations in some region. In a "normal" distribution there should be around 38 % open circles, 24 % thin pluses, 7 % thick pluses and 24 + 7 % minuses.
- 7) Discussion: comparison with earlier work, structural implications etc.

PRESENTATION OF EQUILIBRIUM CONSTANTS, AND THEIR LIMITS OF ERROR

In the standard least square problem, one starts from a measured quantity y , which is an explicit linear function of a number of unknown constants k_i , so that the error square sum, $U = \sum w(y - y_{\text{calc}})^2$, ($w = \text{weight}$), is a second-degree polynomial of the k_i . If the errors in y are only random errors, with a normal distribution, the standard deviations $\sigma(k_i)$ can be strictly defined, as is shown in many standard text-books.

In equilibrium analysis, the measured quantities (such as Z) as a rule are neither linear nor even explicit functions of the sought-for equilibrium constants.

Our LETAGROP computer programs^{8,9} have been designed to calculate the set of values for the unknowns that will minimize the error square sum even in such cases. U is considered as approximately a second-degree function around the minimum, and the standard deviations $\sigma(k_i)$ for the constants are defined by means of their maximum deviations on the "D boundary", which is the curve, surface or super-surface on which $U = U_{\text{min}} + \sigma^2(y)$. For a linear case this definition coincides with the standard one. For a nonlinear case no good definition seems to exist earlier; the LETAGROP approach has the advantage of giving a good graphic picture of the behavior of U , and to give very versatile computer programs.

When quoting values found by the LETAGROP procedure, we have decided to quote, as *error limits, three times the "standard deviation"* for each constant. With a normal distribution this corresponds to a 99.7 % confidence level. We have the experience, comparing the results of LETAGROP treatment with those of graphical treatment, especially curve-fitting, that 3σ roughly corresponds to the maximum error estimated graphically.

We always prefer to quote the *logarithms* of equilibrium constants since, in our experience, the ability to think on a logarithmic scale is the beginning of understanding complicated equilibria. Now, the error square sum U cannot be exactly symmetrical around the minimum both in $U(\log \beta)$ and in $U(\beta)$. For small $\sigma(\beta)$ values, of the order of a few per cent of β , the difference is negligible (see example below); in fact, for well-defined equilibrium constants like β_{22} and β_{53} in the following, the same error limits come out whether one gives β or $\log \beta$ as the constant to be varied.

However, if $\sigma(\beta)$ is considerable in comparison with β , the asymmetry cannot be neglected. In such cases we have found $U(\beta)$ to be reasonably symmetrical, but not $U(\log \beta)$. The reader may, for illustration, consider a "non-existent" complex with $\beta = 0 \pm a$, where $U(\beta)$ is symmetrical; the representation $U(\log \beta)$ will then certainly be very unsymmetrical.

Usually we have obtained the results from LETAGROP in terms of β and $\sigma(\beta)$ but want to represent them in terms of $\log \beta$ and $3\sigma(\log \beta)$. We have decided, arbitrarily, to set a limit at $\sigma(\beta) = 0.20 \beta_M$, thus where the standard deviation is 20 % of the "best" value β_M . For lower values we will set:

$$\sigma(\log \beta) = \frac{1}{2} (\log (\beta_M + \sigma(\beta)) - \log (\beta_M - \sigma(\beta))); (\sigma(\beta) \leq 0.20\beta_M)$$

and quote

$$\log \beta = \log \beta_M \pm 3\sigma(\log \beta).$$

For $\sigma(\beta) > 0.20 \beta_M$ we simply quote $\log \beta \approx \log \beta_M$, and also give the maximum value, $\log \beta < \log (\beta_M + 3\sigma(\beta))$.

For a simple example, $\beta + \sigma(\beta) = 1 \pm 0.02$ would give $\sigma(\log \beta) = \frac{1}{2} \log (1.02/0.98) = 0.036$ and we would quote $\log \beta = 0 \pm 0.0258$. This corresponds to the limiting β values 0.942 and 1.061, as compared with 0.940 and 1.060 for $1 \pm 3\sigma(\beta)$. The difference is negligible considering the fact that the U surface is not exactly a second-degree surface.

In the arbitrary limiting case, let us set $\beta_M \pm \sigma(\beta) = 1 \pm 0.20$. We will then have $\sigma(\log \beta) = \frac{1}{2}(\log 1.20 - \frac{1}{2} \log 0.80) = 0.088$, and $\log \beta \pm 3\sigma(\beta) = 0 \pm 0.264$. The limits for β would be 0.545 and 1.84 compared with 0.4 and 1.6 for $\beta \pm 3\sigma(\beta)$.

Our convention implies that we never quote larger error limits in $\log \beta$ than ± 0.26 .

AVERAGE COMPOSITION OF HYDROXO URANYL COMPLEXES

Figs. 1 a–f show the average composition of the complexes, (\bar{p}, \bar{q}) , calculated from data in the various media, using the computer program MESAK. Since the $\bar{q}(\bar{p})$ plot is very skew, it has been transformed to a plot of q versus $(2\bar{q} - p)$. The lower right-hand corner in each diagram is the point for the (2,2) complex.

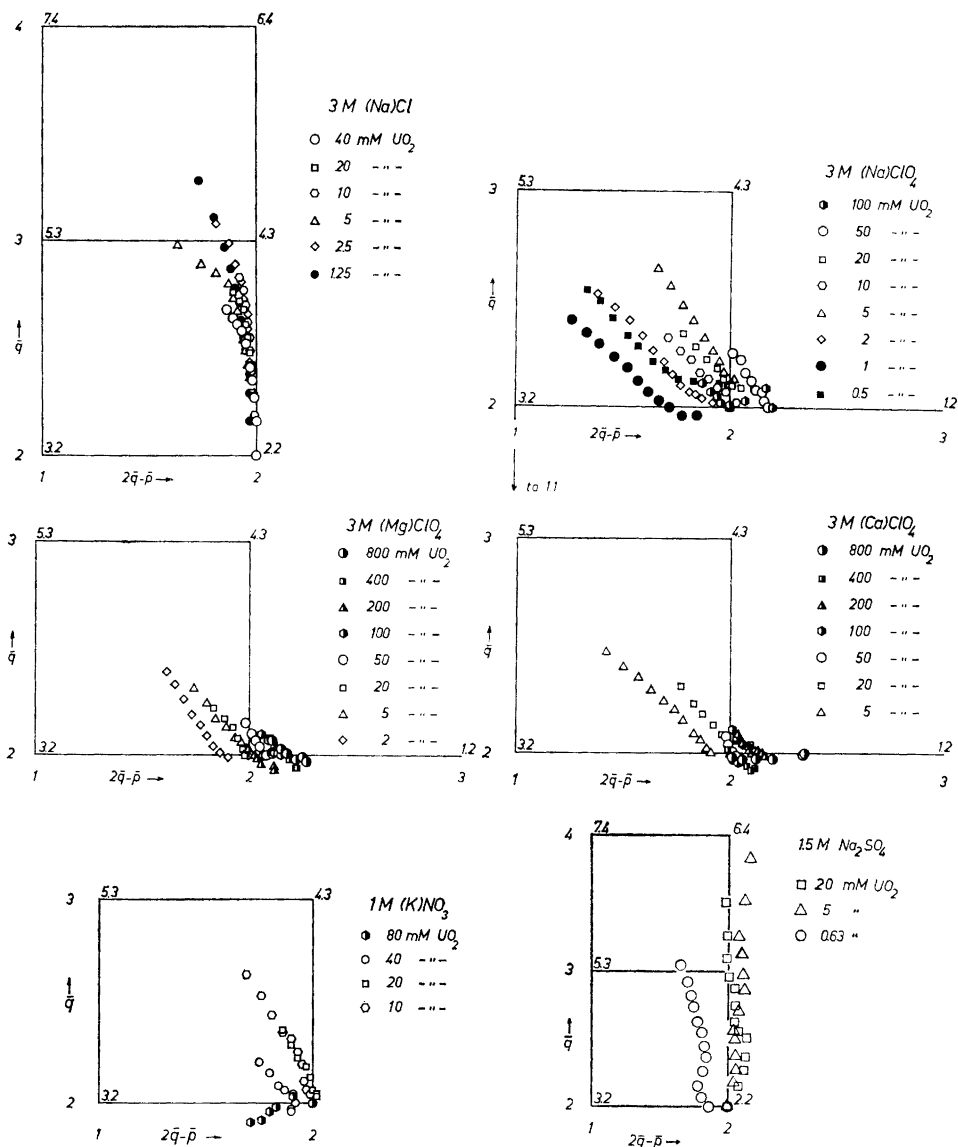


Fig. 1. Hydrolysis of uranyl ion in various media. Average composition of the complexes $\bar{q}(2\bar{p} - \bar{q})$ calculated by MESAK program directly from data, for the following media: a) 3 M (Na)Cl, b) 3 M (Na)ClO₄, c) 3 M (Mg)ClO₄, d) 3 M (Ca)ClO₄, e) 1 M (K)NO₃, f) 1.5 M (Na)SO₄.

In such a diagram, each possible complex corresponds to one point, at the corner of a square. If the solution contains only two complexes, the average

composition of the complexes in the solution would correspond to a point on the line connecting the points for the two complexes; and correspondingly for mixtures of more than two complexes.

Small experimental errors may cause a certain spread of the points in the MESAK diagram but we think it gives a good starting point for equilibrium analysis. The MESAK diagram may be compared to the Patterson diagram in structure analysis, since it summarizes the experimental data in a more easily interpreted form, without introducing any additional hypothesis.

If the earlier formulation of uranyl hydrolysis had been exactly true with only "core and links" complexes ($2n, n+1$), all points would have been on a vertical line, going through (2,2), (4,3), (6,4) etc. This is found to be almost true for the data for sulfate medium, and explains why Alf Peterson could describe his data so well with only ($2n, n+1$) complexes. The deviations are strong for perchlorate, where most points are around the straight line between the point for the (2,2) and the (5,3) complexes. The data for NaCl medium are intermediate.

Those for KNO_3 medium resemble the perchlorate data, but there is a shift at the highest B value (0.08). This shift may be due to activity factors since these points were calculated using data from $B = 0.16$ M and the ionic medium was only 1 M. There may also be other complexes.

At the highest B values for the various perchlorate media, a trend toward the (1,2) complex is visible. For the lowest B values, in NaClO_4 medium, there is some trend toward (1,1). These observations on the MESAK diagrams were supported by the detailed calculations with LETAGROP.

EQUILIBRIUM CONSTANTS FROM LETAGROP TREATMENT

In separate papers, the experimental data, and details of the LETAGROP treatment will be given. Table 1 gives a survey of the "best" sets of equilibrium constants arrived at for the various media. Usually the constants have been calculated using data with total uranyl concentrations B that have been small, at most 0.1 M, in comparison with the medium concentration, usually 3 M.

Only for magnesium and calcium perchlorate medium, the set of constants was made to give the best fit over the whole concentration range, from $B = 1.2$ M to 0.001 M or less. The fact that a reasonable fit can be achieved, and that the data for Ca and Mg medium are very similar, indicates that the activity coefficients vary surprisingly little over the whole concentration range, when UO_2^{2+} is replaced by the bivalent Ca^{2+} or Mg^{2+} . (With Na^+ certainly no set of constants could be made to fit the whole range in B .)

If there had been exactly no change in the activity factors, one would have expected the $\log \beta_{pq}$ values for the Ca and Mg system to come out as the same within the limits of error. This is so for β_{22} , which is important for all B values, and for β_{12} , which is important in the range with high B and little Mg or Ca. However, for β_{53} there are deviations, indicating that for at least one of the systems there are variations in the activity factors of the order of

Table I. Survey of "best" combinations of equilibrium constants for uranyl hydrolysis, for various media. Explanation, see text.

Medium	$\log \beta_{12}$	$\log \beta_{22}$	$\log \beta_{43}$	$\log \beta_{53}$	$\log \beta_{67}$	other species
3 M (Na)Cl	—	-6.64 ± 0.04	-12.54 ± 0.08	-18.07 ± 0.11	-19.96 ± 0.21	$\log \beta_{74} = -24.91 + 0.22$
3 M (Mg)ClO ₄	-3.81 ± 0.16	-6.25 ± 0.03	$\approx -13.33 (< -13.05)$	-17.18 ± 0.04	$\approx -20.18 (< -19.64)$	—
3 M (Ca)ClO ₄	-3.96 ± 0.25	-6.20 ± 0.02	$\approx -13.44 (< -13.21)$	-16.91 ± 0.03	—	—
3 M (Na)ClO ₄	-3.7 (nv) ^a	-6.02 ± 0.02	$\approx -13.83 (< -12.85)$	-16.54 ± 0.03	$\approx -19.21 (< -18.90)$	—
1 M (K)NO ₃	$\approx -4.16 (< -3.45)$	-6.04 ± 0.02	$\approx -13.21 (< -12.97)$	-16.53 ± 0.03	—	$\log \beta_{11} \approx -6.10 (< -5.86)$
1.5 M (Na)SO ₄	—	-5.96 ± 0.04	$\approx -12.79 (< -12.46)$	-16.21 ± 0.05	—	—
		-8.20 ± 0.03	-16.21 ± 0.06	-22.13 ± 0.05	-24.56 ± 0.14	$\log \beta_{8,5} = -32.30 \pm 0.08$
		(-8.17 ± 0.01)	(-16.20 ± 0.03)	(—)	(-24.51 ± 0.09)	(-32.14 ± 0.02)

^a nv = not varied.

0.1 logarithmic unit. A still better fit might have been obtained by restricting oneself to lower B values as was done for NaClO_4 medium.

The values for Na_2SO_4 medium are a LETAGROP refinement of Peterson's data, with the addition of the (5,3) species. Peterson's original constants are given in brackets.

EXISTENCE OF INDIVIDUAL COMPLEXES

Equilibrium analysis leads to a formal description, "the equilibrium data can be explained assuming the following reactions, and equilibrium constants: . . ." However, assuming that the data do not contain important systematic errors, one may ask which of the complexes are really present. We may summarize our present standpoint as follows:

As to the existence of the (2,2) complex, $(\text{UO}_2)_2(\text{OH})_2^{2+}$, there seems to be little doubt: the equilibrium analysis independently indicates it in all media, with well-defined equilibrium constants. The same is true for the (5,3) complex, $(\text{UO}_2)_3(\text{OH})_5^+$, which also comes out with a well-defined constant, especially in the perchlorate media.

The (1,2) complex, $(\text{UO}_2)_2\text{OH}^{3+}$, has been necessary to explain the data in self-medium;⁵ in 3 M $(\text{Na})\text{ClO}_4$ self-medium ($B = 1.4$), we have earlier found $\log \beta_{12} = -3.68 \pm 0.20$, which agrees well with the present results. The present data at the highest B values give a decidedly worse fit if the (1,2) complex is not added, and we would consider this species as well established.

The $(2n, n+1)$ species other than (2,2), thus (4,3), (6,4) etc, offer a more difficult problem. In sulfate medium, Peterson's data indicate these species to be the dominating part of the picture. In chloride medium, the (4,3) species is strongly indicated, and probably also (6,4) exists. It should be pointed out that in perchlorate medium, the data can be interpreted in several alternative ways, with approximately equally good fit: with only (4,3), with only (6,4), with both (4,3) and (6,4), or with an unlimited series. If all $(2n, n+1)$ complexes but (2,2) are left out, however, the agreement is decidedly worse; so, we must conclude that some of these complexes exist, but would not like to commit ourselves to state which of them predominate in perchlorate medium.

The addition of the (7,4) species certainly gives an improved fit for 3 M $(\text{Na})\text{Cl}$ medium. This species, however, is not supported as yet by data from other media, and we regard the assumption as tentative since a similar improvement might be achieved also by adding some other complex or group of complexes, perhaps of the general formula $(2n+1, n+1)$. At least, (7,4) at present seems to be the simplest explanation of the facts.

The (1,1) complex gets some support from our data for very low B in NaClO_4 medium. However, we have not yet reached the "mononuclear wall", and even in 0.00025 M UO_2^{2+} , the polynuclear complexes seem to be dominating. For $(\text{Mg})\text{ClO}_4$ medium, the introduction of β_{11} gave a small improvement but not conclusive.

Recently, Baes and Meyer¹¹ from emf measurements at 96°C have concluded that the (1,1) species UO_2OH^+ is more important at higher temperatures, and we are inclined to think that it really exists. However, most of the β_{11} values quoted in literature, of the order of $10^{-4.0}$ to -5 , have been obtained by neglect-

ing the existence of polynuclear complexes in solutions where the polynuclear complexes would dominate; consequently these values are much higher than the true β_{11} . For references the reader is again referred to "Stability constants".¹

Rush, Johnson and Kraus¹⁰ from their glass electrode data calculated at 25°C, 1 M (Na)Cl medium, $\log \beta_{22} = -6.17$, $\log \beta_{43} = -12.33$, $\log \beta_{53} = -17.00$. Also from glass electrode data at 25°C, in the medium 0.5 M (K)NO₃, Baes and Meyer¹¹ found $\log \beta_{11} = -5.7$, $\log \beta_{22} = -5.92$, $\log \beta_{53} = -16.22$. Rush and Johnson¹² for 1 M (Na)ClO₄ medium at 25°C, found $\log \beta_{22} = -5.91$, $\log \beta_{53} = -16.43$ from their glass electrode data alone; from a combination of glass electrode and spectral data their figures are -5.94 and -16.41 . Recalculation of Ahrlund's data¹⁰ for 1 M (Na)ClO₄ gave at 20°C, $\log \beta_{22} = -5.96$, $\log \beta_{53} = -16.24$, and some evidence for $\log \beta_{11} \approx -4.77$.

The agreement with our values is reasonable, if one considers that the Oak Ridge group worked with weaker ionic media. It seems that we have independently reached the same conclusions about the main species, with the exception that the Oak Ridge group has not found evidence for the (1,2) complex. This is not surprising since they have been working at rather low B values, and it becomes important only at higher B . We also think that from our emf data, which cover a broader range and are not less accurate, it is possible to conclude that at least some of the higher ($2n, n + 1$) complexes exist.

The ΔH values for formation of the (2,2) and (5,3) complexes in 0.5 M (K)NO₃, determined by Baes and Meyer¹¹ from the temperature coefficient between 25° and 94.4°, 10.2 and 25.1 kcal/mole, correspond as well as could be expected with those determined calorimetrically by Schlyter for 3 M (Na)ClO₄ medium (9.55 and 25.7 kcal).

In the discussion of our present equilibrium data one has to remember one limitation on equilibrium analysis, as compared to structure analysis. In the analysis of a crystal structure, the data are transformed to a Patterson diagram, and then finally explained in terms of the positions of the individual atoms. Usually one knows the number of atoms in the unit cell and so if all atoms have been placed, and one has a reasonable agreement with the measured intensities, the structure problem can be regarded as solved, within the limits set by experimental errors. In equilibrium analysis, there is no restriction on the number of species present, and there are reasons to think that in addition to the main species there are many others, in small amounts. Increasing the experimental accuracy, and using a new method may give evidence for more and more species. Whereas there will seldom be any doubt about the main species, there will always be borderline cases which will be questions of judgement and philosophy. (See, for instance, the case of the ($2n, n + 1$) complexes.)

We are certain that in the light of future experience, it will be possible to draw more detailed conclusions on the uranyl hydrolysis reactions from the present data, or from improved data. At present, however, we will not try to carry the equilibrium analysis further.

COMPLEXING WITH THE MEDIUM

The difference between the various media might be ascribed to differences in the complex formation between the medium anion X, on one side, and the uranyl ion and hydroxo uranyl complexes on the other.

If we consider reaction (1), the value for c_{pq} , measured as usually in a medium with the "inert" ions M and X, contains the sum of all concentrations

$$c_{pq} = "[(\text{UO}_2)_q(\text{OH})_p]" = \Sigma[(\text{UO}_2)_q(\text{OH})_p(\text{H}_2\text{O})_x(\text{X})_y(\text{M})_z] \quad (5)$$

Let us assume, that the fraction

$$c_{pq}^0/c_{pq} = \alpha_{pq} \quad (6)$$

of the (p, q) complex in each medium really exists as the uncomplexed hydrated species $(\text{UO}_2)_q(\text{OH})_p(\text{H}_2\text{O})_x$, whereas the remainder of what is reported as " c_{pq} " is complexes with anions of the medium. The corresponding fraction for UO_2^{2+} we denote by $b^0/b = \alpha_0$. The values for α_0 , and α_{pq} , may be thought of as constants in each medium, but may vary widely with the medium.

If we denote by β_{pq}^0 the equilibrium constant of (1), valid for uncomplexed, only hydrated, species, then we have

$$\log \beta_{pq} = \log c_{pq} + p \log h - q \log b \quad (7)$$

$$\log \beta_{pq}^0 = \log c_{pq}^0 + p \log h - q \log b^0 \quad (7a)$$

Now, $\log c_{pq}^0 = \log c_{pq} + \log \alpha_{pq}$ and $\log b^0 = \log b + \log \alpha_0$
hence

$$\log \beta_{pq}^0 = \log \beta_{pq} + \log \alpha_{pq} - q \log \alpha_0 \quad (8)$$

For comparison we shall now make the simplifying assumption that in all our ionic media with Na^+ or K^+ ions, β_{pq}^0 has the same value, so that the differences may be ascribed only to the different complex formation with the medium ions, especially with the negative ion. If we let *unprimed* quantities stand for values in *perchlorate* medium and *primed* quantities stand for some other medium, then one can easily derive

$$\log \alpha_{pq} - \log \alpha'_{pq} = q(\log \alpha_0 - \log \alpha_0') + [\log \beta'_{pq} - \log \beta_{pq}] \quad (9)$$

For a discussion we need estimates for $\log \alpha_0$, the logarithm of the fraction of UO_2^{2+} that is uncomplexed in the various media.

In measurements described in literature a perchlorate medium has usually been used, and one expresses oneself as if α_0 were unity, that is as if there were no perchlorate complexes. Even if this were not true, the usual methods of measuring complex formation give the difference $(\log \alpha_0 - \log \alpha_0')$, which is all we need to know.

We may estimate, from literature data, the first formation constant $\beta_1(\text{Cl}^-, \text{UO}_2^{2+})$, to be approximately 1. In 3 M Cl^- , about $1/4 = 10^{-0.6} = \alpha_0'$ of UO_2^{2+} would be uncomplexed which means $\log \alpha_0 - \log \alpha_0' = 0.6$ in 3 M Cl^- . In similar ways we may estimate $\log \alpha_0 - \log \alpha_0' \approx 0.2$ in 1 M NO_3^- medium, and ≈ 3.3 in 1.5 M SO_4^{2-} medium. We then get the following results, which perhaps indicate the orders of magnitude of the differences.

	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
log α_0 —log α_0'	0.6 (0)	0.2 (0)	3.3 (0)
log α_{22} —log α_{22}'	0.6 (-0.6)	0.3 (-0.1)	4.4 (-2.2)
log α_{43} —log α_{43}'	2.5 (0.7)	1.0 (+ 0.4)	6.9 (-3.0)
log α_{53} —log α_{53}'	0.3 (-1.5)	0.3 (-0.3)	4.3 (-5.6)
log α_{64} —log α_{64}'	1.6 (-0.8)?		8.9 (-4.3)?

If the values (log α_0 —log α_0') are changed, there will be a linear shift in all the other differences.

Although too much weight must not be given to such figures, they indicate at any rate (not unexpectedly) that the hydroxo complexes can also form complexes with the medium ions, and that the complex formation for nitrate and for perchlorate is of the same order of magnitude. The sulfate complexing is much larger. It seems remarkable that the (4,3) species and perhaps also the (6,4) species form much stronger chloride than perchlorate complexes.

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