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Studies on the Hydrolysis of Metal Ions

48. The Uranyl Ion in Sodium, Magnesium, and Calcium Perchlorate Medium

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The hydrolysis equilibria of UO_2^{2+} in the media 3 M (Mg)ClO_4, 3 M (Ca)ClO_4 and 3 M (Na)ClO_4 at 25°C have been studied using glass and quinhydrone electrodes. The data are given in Tables 1–3, the corresponding MESAK diagrams in Figs. 1b–1d in paper 46 of this series. Tables 4 and 5 give the "best" sets of β_{pq} obtained by LETAGROP refinement, assuming various sets of species (p, q), with the corresponding standard deviations in Z. The "best" sets chosen are (1) for Mg, and (2) for Ca perchlorate medium; both include the (1,2), (2,2), (4,3) and (5,3) species, the former also (6,4). For $NaClO_4$ medium, the sets (3)–(6) contain (1,2) (not important in this range), (2,2), (4,3) and (5,3). In addition, (4) contains (6,4), (5) contains an unlimited series ($2n$, $n+1$), and (6) contains (1,1). For discussion, see paper 46[1] of this series.

The general background to this work, notations etc. have been dealt with in the introductory paper.[1] The experimental method was emf titrations, a glass or quinhydrone electrode being used. The experimental work on Na and Mg medium was done by S. H. alone, for that on Ca medium the responsibility was shared between S. H. and B. R. L. R.

EXPERIMENTAL

Reagents

Sodium perchlorate was prepared from Na_2CO_3, Merck *p.a.* and $HClO_4$, Kebo *p.a.*, as described previously.[2] The perchlorate was recrystallized from water; in a concentrated solution (≈ 6 M $NaClO_4$), no traces of Cl^- or Fe^{3+} could be detected.

Magnesium and calcium perchlorates were prepared from MgO or $MgCO_3$ (CaO or $CaCO_3$) and $HClO_4$. The solution was treated in the same way as $NaClO_4$, and the salt was recrystallized twice. The tests for Cl^- and Fe^{3+} were negative.

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Sodium perchlorate was analyzed as described previously. Magnesium perchlorate was analyzed by passing the solution through a H^+-saturated cation exchanger and titrating for the acid set free.

Uranyl perchlorate was prepared from a pure sample of UO_3, obtained from AB Atomenergi, Stockholm. After ignition to U_3O_8 at 800−900°C it was dissolved in an excess of $HClO_4$, with the addition of H_2O_2, *p.a.* for oxidation to U(VI). After most of the water had been boiled off, excess acid was removed by heating under an infrared lamp.

Partly hydrolyzed $UO_2(ClO_4)_2$ solutions were needed for the work with Mg or Ca perchlorate medium since $Mg(OH)_2$ and $Ca(OH)_2$ are too sparingly soluble to make addition from a buret practical. The $UO_2(ClO_4)_2$ solution was shaken with an OH saturated anion exchanger Dowex 2−X8. In advance, the Cl^- ions had to be removed from the anion exchanger by repeated saturation with NaOH and washing with $HClO_4$. When no Cl^- could be detected with $AgNO_3$ in the eluate from $HClO_4$ treatment, the anion exchanger mass was again treated with NaOH under N_2, washed with water, and finally added to the uranyl solution.

Sodium hydroxide, 50 % solution was prepared from solid NaOH *p.a.*, Na_2CO_3 was removed by filtering through a Jena G4 glass filter, and the solution was diluted with boiled water, and standardized against recrystallized hydrazine sulfate, Merck *p.a.*

Perchloric acid was prepared by diluting $HClO_4$ *p.a.*, and standardized against recrystallized Tl_2CO_3.

Silver perchlorate was prepared and analyzed as described previously.[3] The Ag, AgCl *electrodes* were made by Brown's method.[4] Beckman glass electrodes were used throughout, together with a valve potentiometer, Radiometer PHM3i. For measurements with the quinhydrone electrode, the electrode was a bright, ignited Pt foil, and the measurements were made with a Cambridge potentiometer.

The usual apparatus with a "Wilhelm" bridge was used and the titrations were made in an oil thermostat at 25 ± 0.1°C in a room thermostated at 25°C.

When a glass electrode was used, the solution in the titration vessel was stirred by bubbling nitrogen gas, which had earlier passed through 10 % NaOH, 10 % H_2SO_4, a bottle with H_2O, and a bottle with the ionic medium. With quinhydrone, the gas might have carried some quinone with it, so a rotating glass stirrer was used.

Procedure

All experiments were carried out as potentiometric titrations with glass or quinhydrone electrodes. The following cells were used:

− glass electrode|uranyl solution|SE +

or

− Pt|quinhydrone + uranyl solution|SE +

The uranyl solution had the following composition:

B M UO_2^{2+}, H M H^+, $(3-2B-H)$ M Na^+ or $(1.5-B-0.5\,H)$ M $Mg^{2+}(Ca^{2+})$, 3 M ClO_4^-

The free hydrogen ion concentration, h, could be calculated from

$$E = E_0 - 59.155 \log h + E_j \quad (1)$$

which is valid at 25°C. The value for E_0 was found to vary with the total uranyl concentration, B. Special titrations were made to study this relationship. In a solution, the hydrogen ion concentration, h, was kept constant at the value 0.02, 0.05, or 0.1 M and the uranyl concentration was varied from 0 to 0.2 M (Fig. 1). For $h = 0.05$ or 0.1 M between $B = 0$ and $B = 0.2$ M, E varied by 4 mV for the glass electrode, and by 3.6 mV for the quinhydrone electrode in 3 M (Na)ClO_4 medium (Fig. 1). E (B) seems to be linear, with the same slope for $h = 0.1$ and 0.05 M. For $h = 0.02$ the slope was steeper since the hydrolysis is no longer negligible.

For every value of B, $(E_0 + E_j)$ was calculated as a function of h from the points with excess acid. At the higher concentrations, $B = 1.2$ to 0.2 M, E_0 and E_j were determined by successive approximations (as described in Ref.[5]) or by LETAGROP least squares adjustment[6,7].

In $NaClO_4$ medium the value for the ratio $E_j/h = j$ (mV/M) was 22 to 23 for $B = 1.2$, 20 to 21 for $B = 0.8$, and 17 to 18 for $B = 0.2$. For $B < 0.1$ M, j was as usual 16.5 mV

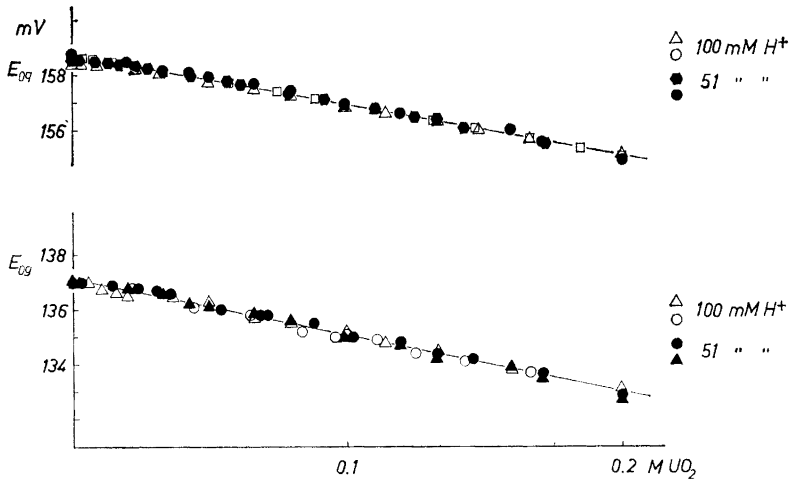

Fig. 1. Variation of E_0 with B. Titration with constant h and varying B. (See text).

M^{-1}. In an earlier paper [5] we found $j = 8$ for $B = 1.4$, but then the salt bridge also contained a solution with $B = 1.4$.

The liquid junction potential $E_j(h)$ for 3 M (Mg or Ca)ClO_4 medium was determined using a hydrogen or Ag, AgCl electrode. Both for Ca and Mg-medium the ratio, j, was 19.0 ± 0.1 mV M^{-1}. For $H > 0.2$ M, slightly lower values, 17 to 18, were observed.

The analytical hydrogen ion excess, H, was known approximately from the analyses but was improved by a Gran extrapolation,[8] for each titration, using the points with excess acid. For $B = 0.2-1.2$ M, the hydrolysis was noticeable so that the Gran extrapolation had an uncertainty of $\pm$ 1 %. In these cases, the correction δ was calculated as described in Ref.[5] or by LETAGROP. Usually it was of the order of $0.4-0.2$ % of the H value, which was in itself a difference between large numbers.

Now that h, H and B were known, we could calculate

$$Z = (h-H)/B \tag{2}$$

Titrations were made in both directions, by adding alkali or partly hydrolysed solution to solutions with acid excess, or by adding acid to a partly hydrolysed solution. With magnesium perchlorate medium, the highest Z values could be reached only by the latter procedure.

Usually equilibrium was obtained within 5 min, but after that we waited about 10 min before the next addition was made.

In special titrations the solutions were made by mixing a partly hydrolysed solution and ionic medium. By interpolation to the B values used in the titrations with constant B, it was found that the points of these special "constant Z" titrations fell on the same curves $Z(\log h)_B$. (Note that Z varied a little with B; it is really H/B that is kept constant).

TREATMENT OF DATA

Our experimental data are given in Tables 1, 2, and 3 and in Figs. 2, 3, and 4. The "constant Z" titrations are represented by points obtained by short interpolation, for the B values used in the "constant B" titrations. For the computer calculations a somewhat smaller number of points were selected. Their distribution can be judged from Fig. 5, 6 and 7.

Table 1. Hydrolysis of uranyl ion in 3 M $(Mg)ClO_4$ medium. The experimental data $(-\log h, Z)_B$ are given, for the points used in the LETAGROP calculations also 1000 $(Z_{calc} - Z)$ with its sign. Z_{calc} was obtained using set (1) of equilibrium constants in Table 4. In the last series B varied, hence B is given for each point.

B = *1.2 M* 1.293, 0.005, −1; 1.326, 0.006; 1.416, 0.008; 1.471, 0.009, −2; 1.534, 0.010; 1.607, 0.012; 1.683, 0.015, −3; 1.862, 0.023; 1.955, 0.029; 2.041, 0.036, −3; 2.236, 0.062; 2.364, 0.089; 2.454, 0.116, + 1; 2.515, 0.136; 2.570, 0.161; 2.620, 0.185; 2.687, 0.221, + 3; 2.723, 0.243; 2.762, 0.268; 2.802, 0.295, + 3; 2.841, 0.327; 2.890, 0.363; 2.916, 0.383, −1; 2.943, 0.405; 2.970, 0.429; 3.008, 0.462, −4; 3.041, 0.488; 3.061, 0.505; 3.108, 0.546, −1; 3.113, 0.553; 0.841, 0.003; 0.935, 0.003; 1.031, 0.004; 1.120, 0.004; 1.580, 0.011;1.856, 0.022; 1.972, 0.029; 2.057, 0.038; 2.185, 0.054; 2.276, 0.070; 2.347, 0.086; 2.446, 0.114; 2.515, 0.139; 2.604, 0.182; 2.681, 0.224; 2.721, 0.251; 2.770, 0.283; 2.806, 0.309; 2.841, 0.337; 2.892, 0.377;

B = *0.8 M* 0.927, 0.000; 0.949, 0.000; 0.969, 0.000; 1.064, 0.002; 1.132, 0.002; 1.246, 0.003; 1.343, 0.004, −1; 1.418, 0.005; 1.517, 0.006; 1.644, 0.009, −2; 1.996, 0.022; 2.232, 0.044; 2.353, 0.064, −2; 2.505, 0.101; 2.594, 0.132, ± 0; 2.655, 0.161; 2.699, 0.183; 2.745, 0.207, −3; 2.790, 0.235; 2.838, 0.266, −5; 2.887, 0.302, −7; 2.941, 0.342; 2.970, 0.365; 3.015, 0.389, + 4; 3.034, 0.416; 3.071, 0.450; 3.120, 0.493, −11; 3.145, 0.516; 3.841, 0.530; 3.188, 0.551, −8; 0.795, 0.001; 0.839, 0.002; 0.902, 0.001; 0.963, 0.002; 1.063, 0.002; 1.183, 0.003; 1.323, 0.004; 1.500, 0.006; 1.720, 0.012; 1.959, 0.021; 2.144, 0.034; 2.271, 0.049; 2.361, 0.063; 2.476, 0.091; 2.559, 0.116; 2.659, 0.159; 2.714, 0.186; 2.764, 0.215; 2.823, 0.251; 2.893, 0.297; 2.933, 0.330; 2.967, 0.356;

B = *0.4 M* 1.015, 0.000; 1.089, 0.000; 1.151, 0.000; 1.247, 0.000; 1.335, 0.002, ± 0; 1.466, 0.002, ± 0; 1.561, 0.003; 1.692, 0.004, ± 0; 1.879, 0.008; 2.349, 0.034, −1; 2.435, 0.045; 2.508, 0.058, −1; 2.571, 0.072; 2.626, 0.087, −1; 2.730, 0.120; 2.816, 0.158; 2.856, 0.179, ± 0; 2.936, 0.225; 2.976, 0.251; 3.015, 0.278, ± 0; 3.095, 0.341; 3.140, 0.376; 3.181, 0.413, −4; 3.230, 0.456; 3.280, 0.502; 3.333, 0.552, −5; 0.936, 0; 1.039, 0.001; 1.159, 0.000; 1.296, 0.000; 1.457, 0.002; 1.678, 0.004; 1.979, 0.010; 2.150, 0.016; 2.283, 0.026; 2.385, 0.037; 2.611, 0.081; 2.772, 0.134; 2.861, 0.181; 2.953, 0.232; 2.983, 0.255; 2.965, 0.293;

B = *0.2 M* 1.389, 0.000; 1.512, 0.000; 1.587, 0.001, + 1; 1.698, 0.001; 1.994, 0.005, ± 0; 2.165, 0.010; 2.560, 0.037, ± 0; 2.761, 0.075; 2.861, 0.106, + 3; 2.928, 0.132; 3.025, 0.182, + 4; 3.101, 0.227; 3.176, 0.282, + 3; 3.254, 0.345; 3.299, 0.380, + 4; 3.339, 0.418; 3.387, 0.460, + 4; 3.433, 0.505; 3.487, 0.556, + 4; 1.476, 0.001; 1.650, 0.001; 1.758, 0.001; 1.881, 0.003; 2.047, 0.006; 2.117, 0.008; 2.205, 0.011; 2.296, 0.015; 2.378, 0.021, −2; 2.514, 0.034; 2.615, 0.048; 2.686, 0.063; 2.751, 0.077; 2.801, 0.091; 2.874, 0.117; 2.934, 0.141; 3.023, 0.185; 3.127, 0.253; 3.199, 0.304; 3.238, 0.335; 3.289, 0.377;

B = *0.1 M* 1.641, 0.003, −2; 1.925, 0.004; 2.360, 0.012, −3; 2.591, 0.020; 2.699, 0.036, −3; 2.790, 0.049; 2.927, 0.080, −2; 3.034, 0.116; 3.127, 0.155, + 2; 3.201, 0.199; 3.274, 0.246, + 1; 3.345, 0.297; 3.413, 0.353, + 3; 3.484, 0.414, + 5; 3.553, 0.481, + 4; 3.587, 0.517, + 2; 3.624, 0.555, + 1; 3.413, 0.353, + 3; 3.741, 0.669, + 10; 2.729, 0.051, −14; 2.363, 0.009; 2.418, 0.011; 2.467, 0.014; 2.522, 0.017; 2.569, 0.021; 2.615, 0.025; 2.726, 0.038; 2.789, 0.048; 2.882, 0.068; 2.949, 0.088; 3.025, 0.116; 3.083, 0.134; 3.129, 0.158;

B = *0.05 M* 2.390, 0.004, + 1; 2.493, 0.008; 2.606, 0.011, + 1; 2.733, 0.019; 2.959, 0.047, + 1; 3.125, 0.089; 3.189, 0.113, + 2; 3.306, 0.165; 3.402, 0.225, + 6; 3.490, 0.291; 3.566, 0.356, + 5; 3.620, 0.407, + 4; 3.664, 0.451, + 3; 3.732, 0.523, ± 0; 3.801, 0.597; 3.861, 0.660, + 4; 3.913, 0.721, + 2; 3.967, 0.788, −3; 4.030, 0.859, −1;
2.309, 0.009; 2.437, 0.015; 2.956, 0.052; 3.079, 0.081; 3.179, 0.116; 3.336, 0.194; 3.468, 0.288; 3.533, 0.340; 3.595, 0.396; 3.566, 0.356, + 5; 3.722, 0.522; 3.788, 0.593; 3.857, 0.671; 3.932, 0.757; 4.014, 0.851;

B = *0.02 M* 2.345, 0.001; 2.441, 0.002, + 1; 2.574, 0.004, ± 0; 2.772, 0.007, + 2; 3.029, 0.026, + 1; 3.260, 0.069, ± 0; 3.348, 0.096, + 1; 3.648, 0.261, + 6; 3.832, 0.425, + 8; 4.006, 0.622, + 5; 4.097, 0.734, + 4; 4.197, 0.858, + 6; 2.629, 0.005; 3.047, 0.029; 3.418, 0.128; 3.490, 0.165, −3; 3.573, 0.216;

B = *0.005 M* 3.095, 0.001, + 8; 3.293, 0.014; 3.519, 0.049, + 8; 3.698, 0.111; 3.844, 0.189, + 6; 3.954, 0.277; 4.055, 0.372, ± 0; 4.150, 0.486, −9; 4.243, 0.604 −11; 4.336 0.724, −4; 4.435, 0.874, −15; 4.544, 1.036, −26; 3.308, 0.012, + 12; 3.507, 0.048; 3.751, 0.137; 3.827, 0.181; 3.883, 0.221, ± 0; 3.656, 0.092; 3.970, 0.293, −2; 4.031, 0.353; 4.118, 0.449; 4.178, 0.513;

B = *0.002 M* 3.238, 0.001; 3.338, 0.003, + 8; 3.458, 0.013, + 6; 3.610, 0.031, + 5; 3.766, 0.068; 3.911, 0.123, + 1; 4.031, 0.193, −4; 4.134, 0.274, + 6; 4.229, 0.365, −5; 4.315, 0.467, −7; 4.400, 0.579, −6; 4.486, 0.701, −3; 4.574, 0.834, −3; 4.681, 0.981, + 10; 4.740, 1.060; 4.809, 1.143, + 20;

B, *−log h*, *Z*, *1000*($Z_{calc}-Z$):
0.000975, 3.456, 0.002, + 7; 0.000975, 3.533, 0.005; 0.000975, 3.618, 0.015; 0.000974, 3.720, 0.028, + 1; 0.000974, 3.948, 0.082; 0.000973, 4.158, 0.180; 0.000972, 4.322, 0.309, + 3; 0.000971, 4.461, 0.459, + 10;
0.000970, 4.566, 0.621; 0.000969, 4.677, 0.794; 0.000969, 4.736, 0.887, + 4; 0.000968, 4.801, 0.985; 0.000968, 4.868, 1.082; 0.000967, 4.936, 1.186, −8; 0.00087, 3.438, 0.002; 0.00087, 3.519, 0.013, −2; 0.00087, 3.626, 0.022; 0.00086, 3.756, 0.037, −7; 0.00086, 3.908, 0.069; 0.00086, 4.062, 0.122; 0.00086, 4.194, 0.193, −13; 0.00086, 4.305, 0.279; 0.00085, 4.403, 0.375, −11; 0.00085, 4.488, 0.476; 0.00085, 4.571, 0.584, + 8; 0.00084, 4.643, 0.705; 0.00084, 4.721, 0.824, + 4; 0.00084, 4.795, 0.948; 0.00084, 4.980, 1.076, + 11; 0.00083, 4.995, 1.225; 0.00083, 5.140, 1.367, + 1;

Table 2. Hydrolysis of uranyl ion in 3 M (Ca)ClO_4 medium. The experimental data (−log h,Z)$_B$ are given, for the points used in the LETAGROP refinement also 1000($Z_{calc}-Z$) with its sign. Z_{calc} was calculated using set (2) of equilibrium constants in Table 4. Points marked with an asterisk were obtained by (short) interpolation from titrations at "constant Z" (really constant H/B).

B = *1.2 M* 3.091, 0.553, −6; 3.058, 0.517; 3.024, 0.483; 2.986, 0.453, + 4; 2.953, 0.425; 2.924, 0.399, + 7; 2.870, 0.354; 2.822, 0.314, + 13; 2.772, 0.280; 2.728, 0.250, + 11; 2.648, 0.206; 2.577, 0.169, + 4; 2.494, 0.135; 2.363, 0.094; 2.160, 0.054, −9; 1.901, 0.026; 1.625, 0.013; 1.524, 0.010, −4; 1.409, 0.007; 1.220, 0.004, −1; 1.125, 0.002; 0.798, 0.001; 0.877, 0.002; 0.973, 0.003; 1.088, 0.003; 1.220, 0.005; 1.411, 0.005; 1.609, 0.010; 1.813, 0.018; 1.975, 0.030; 2.101, 0.042; 2.258, 0.067; 2.361, 0.090; 2.434, 0.111;

B = *0.8 M* 3.179, 0.554, −2; 3.157, 0.534; 3.140, 0.515, + 3; 3.096, 0.449; 3.059, 0.449, −1; 3.029, 0.420; 2.995, 0.393, + 1; 2.964, 0.368; 2.909, 0.324, + 2; 2.858, 0.286; 2.807, 0.253; 2.758, 0.223, −1; 2.718, 0.198; 2.677, 0.174, 2.635, 0.153, + 2; 2.588, 0.135; 2.499, 0.102, −2; 2.398, 0.075; 2.282, 0.053; 2.137, 0.035, −6; 1.959, 0.022; 1.769, 0.014, −6; 1.606, 0.009; 1.484, 0.007, −3; 1.352, 0.005; 0.767, 0.002; 0.841, 0.003; 0.929, 0.002; 1.025, 0.002; 1.262, 0.004; 1.429, 0.005; 1.639, 0.009; 1.886, 0.016; 2.084, 0.029; 2.222, 0.043; 2.319, 0.058; 2.388, 0.072; 2.448, 0.086; 2.531, 0.111; 2.589, 0.134; 2.630, 0.155; 2.707, 0.191; 2.782, 0.235; 2.856, 0.288; 2.910, 0.326; 2.948, 0.354; 3.183, 0.551; 3.137, 0.507; 3.096, 0.468; 3.052, 0.432; 2.980, 0.368; 2.914, 0.315; 2.848, 0.268; 2.792, 0.228; 2.728, 0.192; 2.667, 0.162; 2.601, 0.134; 2.496, 0.098; 2.322, 0.058; 2.065, 0.028; 1.898, 0.018; 1.730, 0.012; 1.100, 0.002; 1.227, 0.003; 1.389, 0.005; 1.598, 0.009; 1.852, 0.016; 1.987, 0.023; 2.074, 0.029; 2.220, 0.045; 2.325, 0.060; 2.396, 0.075; 2.500, 0.104; 2.572, 0.129; 2.638, 0.157; 2.687, 0.182;

B = *0.4 M* 3.308, 0.555, −13; 3.257, 0.507; 3.220, 0.470, −8; 3.176, 0.433; 3.139, 0.399, −7; 3.071, 0.399; 3.037, 0.313, −3; 2.971, 0.265; 2.914, 0.224, ± 0; 2.853, 0.188; 2.795, 0.156, + 1; 2.731, 0.128; 2.630, 0.092, −2; 2.461, 0.052; 2.358, 0.036, −2; 2.217, 0.023; 2.060, 0.014, −3; 1.910, 0.009; 1.777, 0.006; 1.683, 0.004, −1; 1.538, 0.002; 1.438, 0.002; 1.335, 0.001; 1.343, 0.002; 1.554, 0.003; 1.852, 0.007; 2.210, 0.021; 2.427, 0.046; 2.554, 0.071; 2.640, 0.094; 2.753, 0.140; 2.870, 0.198; 2.981, 0.268;

B = *0.2 M* 1.632, 0.002; 1.700, 0.002, ± 0; 1.784, 0.002; 1.884, 0.004, −1; 1.023, 0.007; 2.205, 0.011, −1; 2.401, 0.023; 2.554, 0.041, −4; 2.680, 0.062; 2.773, 0.087, −2; 2.853, 0.114; 2.983, 0.176, −2; 3.042, 0.211; 3.098, 0.248, −3; 3.161, 0.289; 3.213, 0.333, −2; 3.264, 0.382; 3.328, 0.434, −4; 3.386, 0.491; 3.450, 0.555, −11; 1.255, 0.000; 1.384, 0.000; 1.531, 0.002; 1.650, 0.001; 1.959, 0.005; 2.387, 0.021; 2.652, 0.055; 2.777, 0.089; 2.863, 0.119; 2.993, 0.181; 3.068, 0.227;

B = *0.1 M* 3.595, 0.555, −4; 3.555, 0.511, −1; 3.509, 0.471, −6; 3.473, 0.434, −3; 3.435, 0.399, −3; 3.404, 0.366, + 2; 3.335, 0.307, + 3; 3.271, 0.256, + 5; 3.201, 0.210; 3.140, 0.170, + 6; 3.064, 0.134; 2.968, 0.094, + 3; 2.851, 0.061; 2.608, 0.024, ± 0; 2.315, 0.008; 2.101, 0.003, ± 0; 1.964, 0.002; 1.869, 0.001, + 1; 1.938, 0.001; 2.145, 0.003; 2.298, 0.006; 2.508, 0.017; 2.806, 0.053, ± 0; 2.958, 0.091; 3.046, 0.126; 3.157, 0.182; 3.210, 0.216;

B = *0.05 M* 3.729, 0.563; 3.658, 0.473; 3.566, 0.389; 3.480, 0.312, −3; 3.392, 0.241; 3.289, 0.175, ± 0; 3.167, 0.115; 2.998, 0.062, −2; 2.733, 0.023; 2.432, 0.007; 2.229, 0.002; 2.084, 0.001; 4.041, 0.912, + 4; 3.940, 0.800, −8; 3.852, 0.697, −10; 3.773, 0.601, −5; 3.698, 0.512, + 3; 3.610, 0.428, −3; 3.533, 0.350, + 4; 3.445, 0.278, + 2; 3.343, 0.211; 3.238, 0.149, −2; 3.096, 0.092; 2.887, 0.044, −5; 2.569, 0.018; 2.312, 0.010, −6; 2.134, 0.009; 2.023, 0.006, −5;

B = *0.020 M* 4.202, 0.913, + 14; 4.148, 0.834, + 21; 4.087, 0.756; 4.033, 0.686, + 17; 3.977, 0.621; 3.930, 0.561, + 14; 3.879, 0.503; 3.827, 0.446, + 12; 3.781, 0.400; 3.729, 0.354, + 5; 3.680, 0.311, + 4; 3.632, 0.264; 3.582, 0.231, + 5; 3.529, 0.195; 3.472, 0.161, + 5; 3.411, 0.130; 3.340, 0.101, + 2; 3.254, 0.075; 3.159, 0.052, −1; 3.044, 0.034; 2.936, 0.020, ± 0; 2.735, 0.008; 2.582, 0.005, ± 0; 2.474, 0.003; 2.391, 0.002, ± 0; 2.219, 0.000; 2.510, 0.004; 2.853, 0.017; 3.198, 0.059; 3.303, 0.088; 3.440, 0.145; 3.560, 0.219; 3.685, 0.317; 3.768, 0.391;

B = *0.010 M* * 4.374, 1.004, + 2; * 4.456, 1.103, + 11 * 4.533, 1.200, + 5;
B = *0.005 M* 4.424, 0.906; 4.375, 0.834; 4.322, 0.768; 4.238, 0.642; 4.153, 0.528; 4.116, 0.474; 4.070, 0.422; 3.984, 0.328, + 3; 3.884, 0.242; 3.769, 0.166, −1; 3.641, 0.098; 3.468, 0.050; 3.271, 0.020; 3.110, 0.006; 4.418, 0.910, −3; 4.353, 0.812, −2; 4.291, 0.724, −6; 4.236, 0.642, −4; 4.134, 0.502, −2; 4.033, 0.383, −1; 3.932, 0.282, + 1; 3.879, 0.237; 3.827, 0.196, + 6; 3.703, 0.126; 3.597, 0.082, + 5; 3.477, 0.048; 3.392, 0.032, + 5; 3.306, 0.020; 3.225, 0.013, + 5; 3.156, 0.007; 3.036, 0.002, + 6; * 4.415, 0.906; * 4.662, 1.231, + 1; * 4.494, 1.013, + 4; * 4.571, 1.113;

B = *0.002 M* * 4.654, 1.034, ± 0; * 4.728, 1.135, + 3; * 4.813, 1.253, −9; * 4.602, 0.927;

B = *0.001 M* 4.689, 0.907, + 4; 4.643, 0.818, + 17; 4.562, 0.689; 4.511, 0.608, + 7; 4.429, 0.490; 4.376, 0.416, + 1; 4.275, 0.314, −15; 4.205, 0.249; 4.084, 0.164, −14; 3.925, 0.099; 3.815, 0.063, −12; 3.707, 0.045; 3.563, 0.029, −12; 3.421, 0.016; 3.267, 0.011, −6; 4.740, 0.964; 4.621, 0.776; 4.511, 0.601; 4.395, 0.440; 4.261, 0.295; 4.084, 0.170; 3.859, 0.083; 3.637, 0.041, −18; 3.467, 0.025; 3.343, 0.018, −12; 3.250, 0.012; 3.064, 0.002, ± 0; * 4.926, 1.288, −38; * 4.777, 1.072, −22; * 4.853, 1.169;

Table 3a. Hydrolysis of uranyl ion in 3 M $(Na)ClO_4$ medium, B = 1.2 to 0.2 M. The experimental data $(-\log h, Z)_B$ are given, for the points used in the LETAGROP refinement also $1000(Z_{calc}-Z)$ with its sign. Z_{calc} was obtained using the special equilibrium constants in Table 5; for B = 0.2 M the last of the three sets was used.

B = *1.2 M* 3.125, 0.5457, ± 0; 3.100, 0.5242, + 1; 3.071, 0.5038, −1; 3.046, 0.4844, −1; 3.025, 0.4658, + 1; 2.976, 0.4309, −1; 2.936, 0.3993, ± 0; 2.899, 0.3699, + 2; 2.858, 0.3427, ± 0; 2.823, 0.3177, + 1; 2.785, 0.2947, −2; 2.753, 0.2732, −1; 2.719, 0.2531, −2; 2.691, 0.2342, + 1; 2.662, 0.2167, + 2; 2.630, 0.2002, + 1; 2.599, 0.1846, + 1; 2.567, 0.1702, ± 0; 2.535, 0.1562, ± 0; 2.484, 0.1372, −2; 2.445, 0.1195, + 1; 2.410, 0.1085, ± 0; 0.728, 0.0006; 0.768, 0.0005; 0.806, 0.0023; 0.851, 0.0020, −1; 0.899, 0.0024,

-1; 1.002, 0.0033, -1; 1.128, 0.0039, -1; 1.296, 0.0043, $\pm$ 0; 1.384, 0.0061, $\pm$ 0; 1.494, 0.0077, $\pm$ 0; 1.612, 0.0103, $\pm$ 0; 1.730, 0.0142, $\pm$ 0; 1.837, 0.0192, $\pm$ 0; 2.063, 0.0381, $\pm$ 0; 2.163, 0.0514, $\pm$ 0; 2.234, 0.0644, $\pm$ 0; 2.297, 0.0770, $\pm$ 0;

$B = 0.8$ *M* 3.119, 0.4985, + 3; 3.090, 0.4785, -1; 3.048, 0.4430, + 1; 3.004, 0.4119, -2; 0.970, 0.3850, -2; 2.921, 0.3504, -4; 2.864, 0.3045, + 1; 2.812, 0.2684, + 2; 2.795, 2.2572, + 2; 2.761, 0.2362, + 2; 2.703, 0.2080, -4; 2.644, 0.1745, -1; 2.595, 0.1530, -2; 2.540, 0.1277, $\pm$ 0; 2.495, 0.1105, + 1; 0.831, 0.0005; 0.856, 0.0020; 0.889, 0.0014; 0.922, 0.0008; 0.988, 0.0011, $\pm$ 0; 1.057, 0.0024, -1; 1.227, 0.0041, -2; 1.456, 0.0061, -1; 1.759, 0.0131, -2; 2.050, 0.0285, -2; 2.224, 0.0482, -1; 2.339, 0.0677, $\pm$ 0; 2.412, 0.0862, $\pm$ 0; 2.478, 0.1033, + 2; 2.501, 0.1113, + 2; 2.543, 0.1266, + 2; 3.238, 0.6007, -1; 3.210, 0.5769, $\pm$ 0; 3.183, 0.5550, -1; 3.139, 0.5154, + 3; 3.078, 0.4654; 3.025, 0.4241; 0.969, 0.0014; 1.035, 0.0034; 1.282, 0.0044; 1.522, 0.0069; 1.828, 0.0151; 2.091, 0.0311; 2.300, 0.0597; 3.117, 0.4985; 3.083, 0.4696; 3.051, 0.4430; 3.0169, 0.4170; 2.988, 0.3949; 2.965, 0.3732; 2.912, 0.3341; 2.863, 0.3000; 2.817, 0.2695; 2.779, 0.2420; 2.735, 0.2178; 2.694, 0.1958; 2.635, 0.1608;

$B = 0.4$ *M* 1.105, 0.0007, $\pm$ 0; 1.328, 0.0010, + 1; 1.554, 0.0027, + 1; 1.644, 0.0047, $\pm$ 0; 1.754, 0.0063, $\pm$ 0; 1.878, 0.0089, $\pm$ 0; 1.969, 0.0120, $-$ 1; 2.057, 0.0160, -1; 2.139, 0.0209, -1; 2.221, 0.0261, $\pm$ 0; 2.325, 0.0382, $\pm$ 0; 2.416, 0.0503, + 2; 3.319, 0.5989, -3; 3.289, 0.5671, $\pm$ 0; 3.230, 0.5140, -3; 3.203, 0.4820, + 4; 3.122, 0.4175, -4; 3.068, 0.3681, $\pm$ 0; 2.980, 0.2987, $\pm$ 0; 2.888, 0.2416; 2.821, 0.1977; 2.710, 0.1402; 2.632, 0.1075; 2.516, 0.0723; 1.884, 0.0084; 3.303, 0.5770, + 3; 3.255, 0.5326, + 2; 3.193, 0.4767, $\pm$ 0; 3.142, 0.4313, $\pm$ 0; 3.086, 0.3825, $\pm$ 0; 3.027, 0.3346, $\pm$ 0; 2.981, 0.2968, + 3; 2.904, 0.2458, $\pm$ 0; 2.784, 0.1748, $\pm$ 0; 2.711, 0.1387, $\pm$ 0; 2.599, 0.9680, $\pm$ 0; 2.501, 0.6980, $\pm$ 0; 1.013, 0.0000; 1.106, 0.0001; 1.325, 0.0017; 1.554, 0.0028; 1.644, 0.0047; 1.754, 0.0063; 1.874, 0.0093; 1.968, 0.0121; 1.059 0.0159; 2.141, 0.0209; 2.219, 0.0261; 2.328, 0.0381; 2.418, 0.0502; 3.296, 0.5770; 3.253, 0.5352; 3.175, 0.4613; 3.103, 0.3695; 3.036, 0.3405; 2.946, 0.2688; 2.851, 0.2085; 2.791, 0.1734; 2.726, 0.1419; 2.618, 0.1009; 2.490, 0.0646; 2.438, 0.0542; 2.379, 0.0443;

$B = 0.2$ *M* 1.343, 0.0006, $\pm$ 0; 1.497, 0.0021, -1; 1.696, 0.0028, -1; 2.109, 0.0099, -1; 2.318, 0.0204, $\pm$ 0; 2.496, 0.0390, + 1; 2.626, 0.0630, + 2; 2.724, 0.0903, + 3; 2.808, 0.1209, + 4; 3.000, 0.2247, + 4; 3.112, 0.3065, + 3; 3.148, 0.3361, + 3; 3.187, 0.3700, + 2; 3.244, 0.4230, $\pm$ 0; 3.313, 0.4881, + 1; 3.373, 0.5478, + 3; 3.444, 0.6193, + 10; 3.247, 0.4126, + 13; 3.418, 0.5930, + 7; 3.484, 0.6616, + 14; 3.526, 0.7203, + 5; 3.566, 0.7682, + 6; 1.717, 0.0027, $\pm$ 0; 2.209, 0.0168, -3; 2.472, 0.0405, -4; 2.638, 0.0717, -3; 2.751, 0.1027, $\pm$ 0; 2.873, 0.1521, + 3; 2.976, 0.2140, -1; 3.066, 0.2749, $\pm$ 0; 3.179, 0.3589, + 6; 3.328, 0.5015, + 3; 3.457, 0.6260, + 18; 1.419, 0.0012; 1.544, 0.0016; 1.752, 0.0021; 2.145, 0.0110; 1.264, 0.0009; 1.330, 0.0015; 1.418, 0.0017; 1.542, 0.0023; 1.746, 0.0034; 2.140, 0.0113; 3.309, 0.4640; 3.210, 0.3719; 3.110, 0.2905; 3.008, 0.2183; 2.893, 0.1553; 2.760, 0.0994; 2.079, 0.0096; 1.580, 0.0001; 3.247, 0.4126; 3.418, 0.5930; 3.484, 0.6616; 3.526, 0.7203; 3.566, 0.7682; 3.222, 0.4128; 3.412, 0.5930; 3.474, 0.6617; 3.525, 0.7203; 3.567, 0.7682;

Table 3b. Hydrolysis of uranyl ion in 3 M (Na)ClO_4 medium, $B = 0.1$ to 0.00025 M. The data $(-\log h, Z)_B$ are given, for the points used in the LETAGROP refinement also the values of $1000(Z_{calc}-Z)$, with its sign. The first Z_{calc} was calculated with the set (4) of equilibrium constants in Table 5, the second with set (6), which also includes the (1,1) complex. Points marked out with an asterisk were obtained by interpolation of titrations at "constant Z" (really constant H/B).

$B = 0.1$ *M* 1.877, 0.003; 2.204, 0.006; 2.517, 0.021; 2.755, 0.051; 2.868, 0.087, + 8, -2; 3.044, 0.159; 3.096, 0.190; 3.183, 0.247, + 11, + 5; 3.243, 0.296, + 6, + 2; 3.292, 0.338, + 3, + 1; 3.335, 0.376, + 1, $\pm$ 0; 3.394, 0.424; 3.485, 0.511; 3.541, 0.572, + 3, + 6; 3.602, 0.637; 3.642, 0.683, + 3, + 2; 3.671, 0.716; 3.700, 0.749, + 3, + 1; * 3.357, 0.404, -8, -8; 2.036, 0.002; 2.419, 0.014, + 4, -2; 2.901, 0.099; 3.060, 0.172, + 8, -1; 3.160, 0.235; 3.262, 0.312; 3.335, 0.374; 3.410, 0.455, -10, -9; 3.472, 0.515; * 3.115, 0.208, + 5, -3;

B = 0.05 M * 3.692, 0.604, −12, −11; * 3.507, 0.406, −4, −4; * 3.271, 0.210; * 3.267, 0.210, + 3, −3; 1.852, 0.004; 2.062, 0.004; * 3.864, 0.807, −9, −12; 2.393, 0.009, −1, −3; 2.638, 0.020; 2.858, 0.046; 2.995, 0.080; 3.098, 0.116, + 7, −1; 3.232, 0.183; 3.338, 0.254; 3.478, 0.374; 3.588, 0.481, ± 0, + 1; 3.654, 0.552; 3.710, 0.616; 3.808, 0.728; 3.923, 0.867; 4.011, 0.976, + 6, −2; 4.047, 1.066; 2.041, 0.000; 2.138, 0.000; 2.375, 0.006; 2.667, 0.024; 2.902, 0.058, + 2; −5; 3.041, 0.098; 3.171, 0.155; 3.262, 0.209; 3.380, 0.297, −4, −7; 3.492, 0.391; 3.560, 0.460; 3.622, 0.525; 3.663, 0.573; 3.720, 0.638, −14, −13;

B = 0.02 M * 3.472, 0.217; * 3.477, 0.216, + 5, + 1; * 4.032, 0.809, −4, −6; * 3.890, 0.626, −6, −6; * 3.710, 0.410, + 7, + 7; 2.667, 0.002, + 8, + 6; 3.008, 0.031; 3.252, 0.089, + 14, + 9; 3.392, 0.159, + 9, + 4; 3.578, 0.288; 3.756, 0.462; 3.881, 0.611; 3.984, 0.747; 4.116, 0.919; 4.226, 1.058, + 4, ± 0; 4.322, 1.175; 4.408, 1.273, −7, −9; 2.238, 0.000; 2.336, 0.006; 2.608, 0.010; 2.971, 0.037, −3, −6; 3.244, 0.094; 3.490, 0.219; 3.563, 0.274; 3.622, 0.323, + 11, + 9; 3.673, 0.368, + 13, + 12; 4.133, 0.930; 3.981, 0.727; 3.840, 0.546, + 13, + 14; 3.678, 0.381; 3.602, 0.301; 3.330, 0.122, + 14, + 9; 3.007, 0.028; 2.572, 0.004;

B = 0.010 M * 3.182, 0.043, ± 0, −3; * 3.240, 0.055, −1, −4; * 3.620, 0.224; * 3.634, 0.232, −5, −8; * 3.718, 0.300, −8, −10; * 3.846, 0.414, −1, −1; * 3.905, 0.486, −8, −7; * 4.055, 0.652, + 15, + 16; * 4.051, 0.665; 4.123, 0.770; * 4.155, 0.811, −4, −4; * 4.291, 1.000, −1, −3; * 4.383, 1.120, −1, −3; * 4.567, 1.345, −27, −27; 2.496, 0.004; 2.669, 0.007; 2.726, 0.011; 2.778, 0.010, −2, −3; 2.909, 0.015; 3.052, 0.027, −2, −4; 3.205, 0.047; 3.321, 0.076; 3.428, 0.107; 3.570, 0.177; 3.671, 0.248; 3.756, 0.314; 3.822, 0.378; 2.637, 0.006; 2.838, 0.009; 3.117, 0.028; 3.357, 0.081; 3.516, 0.149, + 5, + 1; 3.631, 0.220; 3.722, 0.292; 3.869, 0.435; 3.977, 0.568; 4.121, 0.759; 4.280, 0.986; 4.440, 1.192; 2.462, 0.003; 2.633, 0.009; 2.883, 0.017; 3.222, 0.051; 3.462, 0.126; 3.614, 0.213; 3.729, 0.300; 3.818, 0.386; 3.964, 0.551; 4.074, 0.702; 4.182, 0.847;

B = 0.005 M 2.814, 0.008, −3, −4; 3.019, 0.016, −5, −5; 3.286, 0.039; 3.422, 0.062; 3.522, 0.095; 3.619, 0.129; 3.688, 0.166; 3.749, 0.203; 3.844, 0.275; 3.921, 0.342; 3.979, 0.406; * 3.407, 0.058, −1, −2; * 3.455, 0.070, ± 0, −2; * 3.638, 0.140, −1, −3; * 3.810, 0.230, + 19, +17; * 3.783, 0.233; * 3.877, 0.308, −3, −3; * 3.987, 0.420, −3, −3; * 4.048, 0.494, −5, −4; * 4.187, 0.672, + 4, + 6; * 4.232, 0.728; * 4.253, 0.778; * 4.278, 0.814, −3, −2; * 4.412, 1.003, + 6, + 5; * 4.502, 1.122, + 9, + 8; * 4.690, 1.347, −11, −11; 2.892, 0.004; 3.377, 0.051; 3.440, 0.064; 3.494, 0.080; 3.590, 0.113; 3.724, 0.185; 3.825, 0.255; 3.960, 0.385; 4.055, 0.498; 4.163, 0.641; 4.205, 0.702; 4.276, 0.810; 4.337, 0.905; 4.456, 1.074; 4.550, 1.198; 4.626, 1.292; 2.672, 0.008; 3.739, 0.190; 3.930, 0.365; 4.057, 0.490; 4.163, 0.629; 4.341, 0.886; 4.503, 1.114; 4.677, 1.317;

B = 0.002 M * 3.337, 0.022, −4, −4; * 3.705, 0.086, −1, −1; * 3.741, 0.097, + 1, ± 0; * 3.866, 0.162, −6, −6; * 3.872, 0.167, −7, −8; * 4.008, 0.249, + 7, + 7; * 3.989, 0.251; * 4.088, 0.330, ± 0, + 1; * 4.180, 0.430, + 4, + 6; * 4.239, 0.500, + 11, + 13; * 4.365, 0.687, + 12, + 13; * 4.425, 0.790; * 4.442, 0.822, −1, + 1; * 4.571, 1.015, + 7, + 7; * 4.662, 1.135, + 14, + 14; * 4.697, 1.195; * 4.857, 1.355, + 7, + 7; 3.389, 0.009; 3.435, 0.017; 3.517, 0.028; 3.653, 0.056; 3.769, 0.098; 3.867, 0.145; 4.011, 0.253; 4.156, 0.395; 4.212, 0.470; 4.349, 0.676; 4.474, 0.865; 4.588, 1.040; 4.772, 1.277; 4.909, 1.421;

B = 0.001 M 4.817, 1.222; 4.711, 1.074; 4.623, 0.934; 4.542, 0.800; 4.469, 0.672; 4.405, 0.552; 4.314, 0.440; 4.231, 0.336, ± 0, + 2; 4.133, 0.241; 4.013, 0.158, −1, ± 0; 3.882, 0.089, + 6, + 7; 3.734, 0.040; 3.593, 0.021; 3.477, 0.009, + 8, + 9; 3.730, 0.045, + 6, + 7; 4.172, 0.272; 4.379, 0.549; 4.679, 1.030; 4.752, 1.136; 4.819, 1.235; 3.698, 0.044; 3.789, 0.073; 3.893, 0.104; 4.052, 0.191; 4.123, 0.237, −4, −2; 4.229, 0.338; 4.271, 0.388; 4.415, 0.586; 4.530, 0.770; 4.630, 0.942; 4.728, 1.101; 4.843, 1.247; 4.951, 1.384; * 3.635, 0.032, + 2, + 3; * 3.956, 0.130, −4, −2; * 4.043, 0.185, −10, −9; * 4.062, 0.197, −9, −8; * 4.177, 0.266; * 4.166, 0.268, + 3, + 4; * 4.165, 0.268; * 4.247, 0.352, + 2, + 4; * 4.320, 0.445, ± 0, + 2; * 4.381, 0.518, + 13, + 15; * 4.500, 0.707, + 13, +15; 4.553, 0.808; * 4.566, 0.828; * 4.690, 1.034, −4, −3; * 4.783, 1.148; * 4.828, 1.212, + 9, + 8; * 4.980, 1.360, + 18, +17;

B = *0.0005 M* * 3.935, 0.055, + 9, + 12; * 4.149, 0.155, −4, ± 0; * 4.174, 0.172, −5, −2;* 4.222, 0.212, −12, −9; * 4.255, 0.245, −19, −15; * 4.408, 0.394, −6, −3; * 4.525, 0.550, + 9, + 12; * 4.638, 0.740, + 10, + 12; * 4.689, 0.842, −3, −2; * 4.818, 1.060, −7, −8; 4.921, 1.177; * 4.960, 1.237, + 11, + 9; * 5.105, 1.376, + 18, + 15;

B = *0.00025 M* * 4.235, 0.097, + 23, + 29; * 4.376, 0.220, −9, −3; * 4.395, 0.237; * 4.402, 0.250, −17, −11; * 4.458, 0.300, −11, −5; * 4.579, 0.470, −25, −20; * 4.670, 0.610, −16, −13; * 4.782, 0.800, −5, −4; * 4.839, 0.900; * 4.953, 1.115, −28, −31; * 5.097, 1.287, −8, −12; * 5.228, 1.400, + 7, +2;

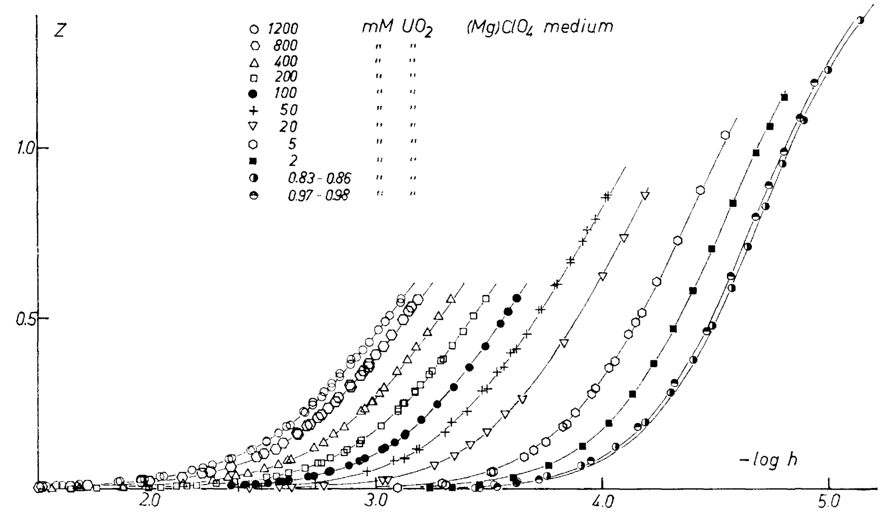

Fig. 2. Hydrolysis of uranyl ion in 3 M $(Mg)ClO_4$ medium. Data $Z(\log h)_B$ and curves, calculated with set (1) of equilibrium constants in Table 4.

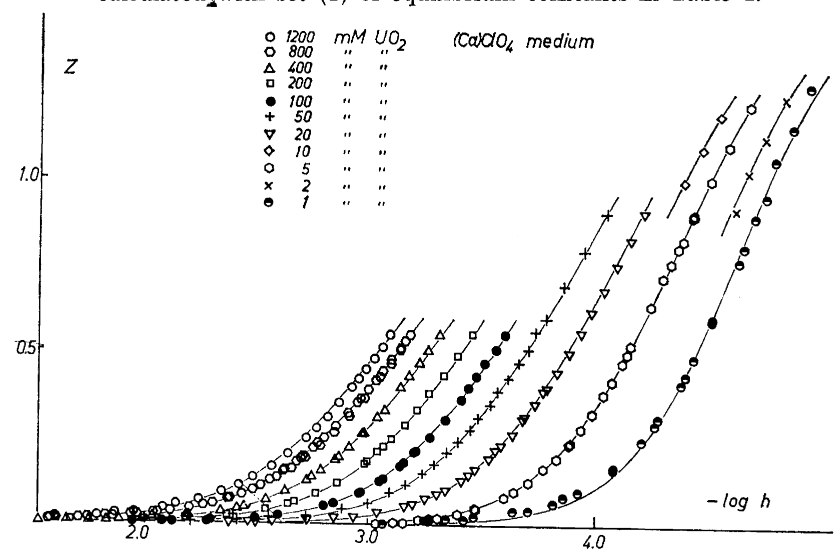

Fig. 3. Hydrolysis of uranyl ion in 3 M (Ca) ClO_4 medium. Data $Z(\log h)_B$ and curves calculated with the set (2) of equilibrium constants in Table 4.

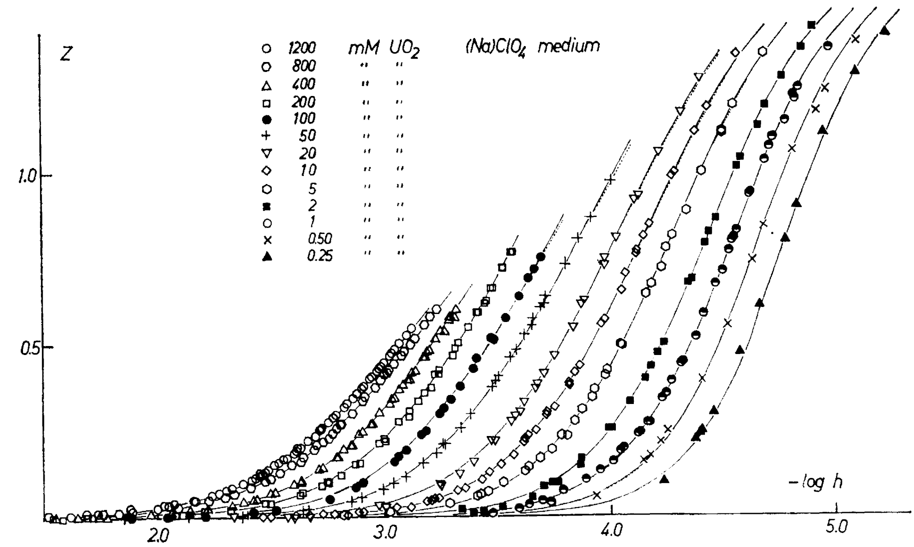

Fig. 4. Hydrolysis of uranyl ion in 3 M (Na)ClO_4 medium: experimental data $Z(\log h)_B$ and calculated curves. For the highest uranyl concentrations, $B = 0.2-1.2$ M, the special constants in Table 4 were used. For the lower concentrations, $B = 0.1-0.00025$ M, the full-drawn curves were calculated with set (4) of equilibrium constants in Table 5, the dotted curves with set (3) (where the (6,4) complex has been left out.)

From the data the average composition of the complexes could be calculated. The MESAK diagram, shown in Ref.[1] Fig 1b—d indicates as main complexes the (2,2) and (5,3) complexes. We shall leave out our calculations by earlier methods (although they gave practically the same result) and conside only the calculations by LETAGROP.

Since the data for calcium and magnesium perchlorate medium were similar but the data for sodium different, it was concluded that the activity coefficients varied but little when the bivalent ions, UO_2^{2+}, Ca^{2+}, and Mg^{2+} were exchanged for each other, so, the data over the whole concentration range $B = 1$ mM to 1200 mM, were treated with the same equilibrium constants. It was then necessary to introduce also the (1,2) complex, which had already been indicated by earlier work with self-medium,[5] and was also indicated by the MESAK diagrams.

In the LETAGROP treatment, we searched for the set of equilibrium constants, with the set of complexes assumed, which minimized the error square sum $U = \Sigma(Z_{calc}-Z_{obs})^2$. The same weight was thus given to each measured point although the program allows weighting. This was justified by the fact that the spread in Z was approximately the same over the whole range of the experiments, so that it was not thought worthwhile to introduce a complicated system of weighting.

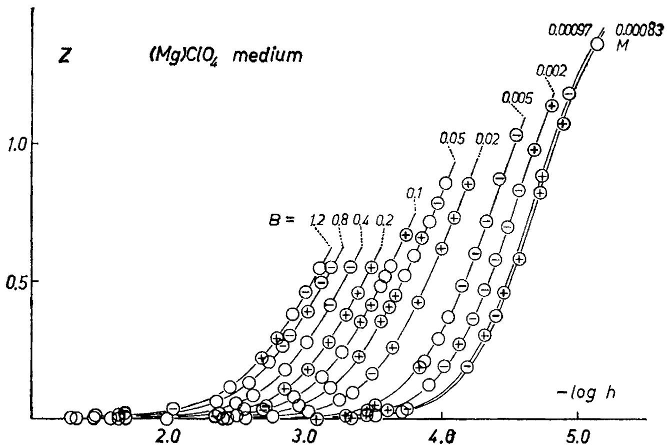

Fig. 5. Uranyl hydrolysis in $(Mg)ClO_4$ medium. Points used for LETAGROP refinement and calculated curves. Signs in circles indicate deviations of Z_{calc} from experimental values; they are thick if the deviation is larger than 1.5 σ, thin if between 0.5 σ and 1.5 σ; *cf*. Table 1.

Table 4 gives a survey of the LETAGROP results with Mg and Ca perchlorate medium; Table 5 gives the results with Na perchlorate medium. The Mg data seem slightly more accurate than the Ca data. It is certainly necessary to assume the (1,2), (2,2), and (5,3) species, which come out with well-defined equilibrium constants. As can be seen from the last column, 1000 $\sigma(Z)$, the agreement is considerably improved by introducing (4,3) or (6,4) or both. To a certain degree, these ($2\,n$, $n+1$) complexes are supplementary so that one can replace the other. We have decided to give, as "best", values, the set,

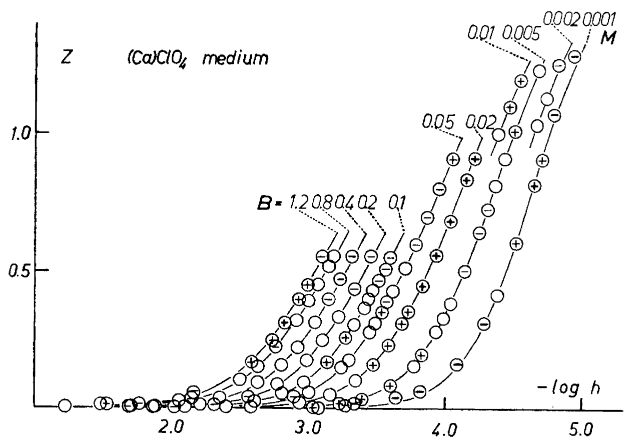

Fig. 6. Uranyl hydrolysis in $(Ca)ClO_4$ medium. Points for LETAGROP, notations as in Fig. 5; *cf*. Table 2.

Table 4. Hydrolysis of uranyl ion in Mg and Ca perchlorate medium. "Best" values for equilibrium constants, from LETAGROP treatment. (n.v. = not varied.)

	$10^4\beta_{12}$	$10^7\beta_{22}$	$10^8\beta_{43}/\beta_{22}$	$10^{11}\beta_{53}/\beta_{22}$	$10^8\beta_{64}/\beta_{22}^2$	$1000\ \sigma(Z)$	
Mg	1.558 ± 0.194	5.612 ± 0.113	8.286 ± 2.59	1.171 ± 0.024	2.11 ± 1.71	6.05	(1) *
all B values	1.648 ± 0.167	5.506 ± 0.069	11.17 ± 9.74	1.193 ± 0.015	—	6.08	
	1.171 ± 0.160	5.970 ± 0.043	—	1.121 ± 0.016	6.815 ± 0.687	6.3	
	1.740 (n.v.)	6.219 ± 0.063	—	1.249 ± 0.027	—	11.3	
0.001 — 0.1 M	—	5.520 ± 0.089	7.9 (n.v.)	1.222 ± 0.025	($10^7\beta_{11}$ = 9.832 ± 3.99)	7.3	
Ca	1.095 ± 0.222	6.383 ± 0.093	5.67 ± 1.31	1.909 ± 0.025	—	7.8	(2) *
all B values	0.7417 ± 0.203	6.669 ± 0.059	—	1.854 ± 0.031	2.673 ± 1.06	8.1	
0.001 — 0.1 M	1.100 (n.v.)	6.743 ± 0.148	−0.367 ± 2.459	1.894 ± 0.045	1.348 ± 1.949	9.4	

Table 5. Hydrolysis of uranyl ion in Na perchlorate medium. "Best" sets of equilibrium constants, according to LETAGROP. (n.v. = not varied.)

B	$10^4\beta_{12}$	$10^7\beta_{22}$	$10^8\beta_{43}/\beta_{22}$	$10^{11}\beta_{53}/\beta_{22}$	$10^9\beta_{64}/\beta_{22}^2$	$100\ \sigma(Z)$	
0.00025	—	9.817 ± 0.165	−4.318 ± 2.983	2.977 ± 0.051	7.610 ± 2.031	9.6	
to 0.100 M	2.0(n.v.)	9.707 ± 0.101	—	3.177 ± 0.048	—	11.0	
	2.0 »	9.194 ± 0.124	9.931 + 1.838	3.180 ± 0.044	—	9.6	(3)
	2.0 »	9.563 ± 0.089	—	3.040 ± 0.045	7.774 ± 1.307	9.4	
	2.0 »	9.499 ± 0.162	1.542 ± 3.420	3.059 ± 0.058	6.816 ± 2.412	9.4	(4) *
	−1.55 ± 1.10	9.598 ± 0.174	2.295 ± 2.75	3.084 ± 0.049	—	9.26	
	—	9.428 ± 0.101	—	3.121 ± 0.040	k_0 = 17.89 ± 4.41	9.2	(5)
	—	9.136 ± 0.154	6.853 ± 1.74	3.208 ± 0.051	$10^7\beta_{11}$ = 7.97 ± 2.91	9.0	(6)
1.2 M	1.675 ± 0.051	6.136 ± 0.079	2.704 ± 2.30	1.116 ± 0.899	—	1.1	
0.8	1.654 ± 0.112	6.989 ± 0.131	3.698 ± 2.94	1.520 ± 0.802	—	2.1	
0.4	1.786 ± 0.160	7.527 ± 0.197	10.31 ± 5.82	2.982 ± 1.26	—	1.7	
0.2	2.443 ± 0.363	8.037 ± 0.165	19.87 ± 2.69	4.06(n.v.)	—	4.8	
	2.787 ± 0.45	7.719 ± 0.208	29.06 ± 3.70	3.05 »	—	5.23	
	1.348 ± 0.341	9.061 ± 0.061	(−3.523 ± 4.20)	6.489 ± 0.457	—	3.7 *	

(1) with both; after conversion to log β and giving $\pm$ 3 $\sigma(\log \beta)$ or the maximum

$$\log \beta_{12} = -3.81 \pm 0.16,\ \log \beta_{22} = -6.25 \pm 0.03,\ \log \beta_{43} \approx -13.33(< -13.05),\ \log \beta_{53} = -17.18 \pm 0.04,\ \log \beta_{64} \approx -20.18\ (< -19.64);\ \text{for 3 M (Mg)ClO}_4\ \text{medium} \quad (1)$$

The last set for Mg was an attempt to introduce β_{11}; only the values for the lowest B, 0.001 to 0.1 M, were used, which is bound to decrease $\sigma(Z)$ somewhat. β_{11} came out as $(10 \pm 4) \times 10^{-7}$, $\log \beta_{11} \approx -6.0\ (< -5.7)$ so that these data give only mild support for the (1,1) species.

For the calcium data, the last set used the lowest concentrations, 0.001—0.1 M. As "best" values we have chosen set (2) which gives

$$\log \beta_{12} = -3.96 \pm 0.25,\ \log \beta_{22} = -6.20 \pm 0.02,\ \log \beta_{43} \approx -13.44\ (< -13.2),\ \log \beta_{53} = -16.91 \pm 0.03;\ \text{for 3 M (Ca)ClO}_4\ \text{medium.} \quad (2)$$

The data for sodium perchlorate medium, Table 5, were divided into two groups. Each B value higher than 0.1 M was treated separately whereas the lowest B values, 0.00025—0.1 M, were treated together.

For $B = 0.4$, 0.8, and 1.2 M, the data gave well-defined constants for the (1,2) and (2,2) complexes, whereas β_{43} and β_{53} ,which are not very important in this range, came out with large deviation values. For Na medium data we could (not unexpectedly) get a better adjustment using four parameters for

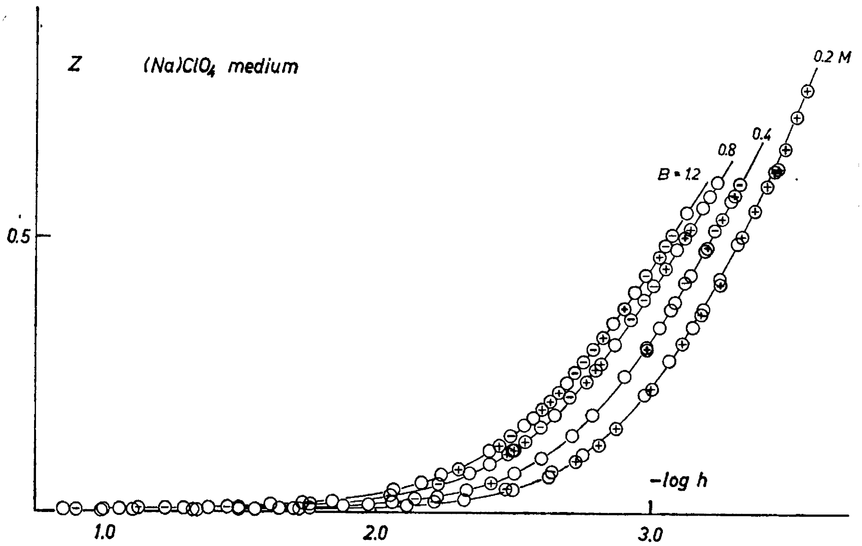

Fig. 7 a. Uranyl hydrolysis in 3 M (Na)ClO$_4$ medium. Points for LETAGROP, notations as in Fig. 5; *cf.* Table 3 a.

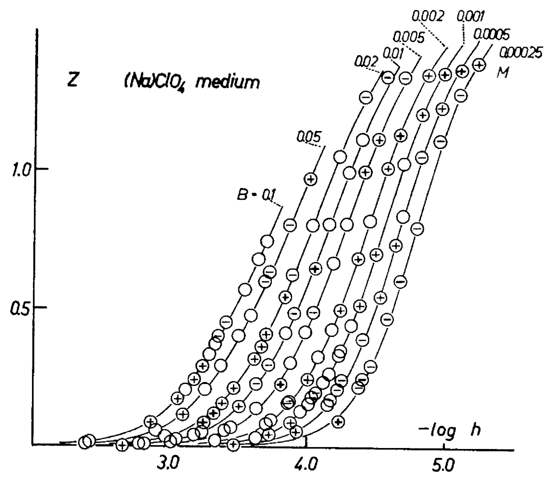

Fig. 7 b. Uranyl hydrolysis in 3 M (Na)ClO$_4$ medium. Points for LETAGROP, notations as in Fig. 5; *cf.* Table 3 b.

data at a single value for B, than over a broad range of B; also, the absolute values of Z are smaller at higher B. Too much weight should not be given to the numerical values for the constants; β_{22} seems to decrease slightly with increasing B, and a similar trend though less pronounced is noticed for the other constants.

For $B = 0.2$ M, three sets are given: the third one in which four equilibrium constants were varied, gave a negative β_{43}; in the first two β_{53} was kept constant at resonable values. In diagram and calculation we have used the last set, however with $\beta_{43} = 0$.

For the lower B values, 0.00025—0.1 M, the (1,2) complex is not important, so β_{12} was either neglected or given a resonable value. Once when we had it varied, it came out negative. Again, (2,2) and (5,3) came out with well-defined equilibrium constants, and again the agreement is improved if (4,3) or (6,4) or both are introduced. As "best" set we decided on (4):

$$(\log \beta_{12} = -3.70),\ \log \beta_{22} = -6.02 \pm 0.02,\ \log \beta_{43} \approx -13.83\ (< -12.85),$$
$$\log \beta_{53} = -16.54 \pm 0.03,\ \log \beta_{64} \approx -19.21\ (< -18.90). \qquad (4)$$

How small the differences are can be judged by Fig. 4, where the full-drawn lines were calculated with set (4), and the broken curves with set (3), where (6,4) is neglected:

$$\log \beta_{12} = -3.7 \text{ (not varied)},\ \log \beta_{22} = -6.04 \pm 0.02,\ \log \beta_{43} = -13.04 \pm 0.24,$$
$$\log \beta_{53} = -16.54 \pm 0.03 \text{ for 3 M (Na)ClO}_4 \text{ medium.} \qquad (3)$$

We would also like to draw the attention to the sets (5) and (6) in Table 5. In set (5), in addition to (5,3) and (2,2), an unlimited series of $(2\ n,\ n + 1)$ species has been assumed with the relationship

$$\log \beta_{2n,n+1} = \log k_0 + n \log k = n \log \beta_{22} - (n-1) \log k_0$$

It really gives a slightly better agreement than "best" one (4) and would correspond to

$$\log \beta_{22} = -6.03 \pm 0.02,\ \log \beta_{53} = -16.63 \pm 0.02,\ \log \beta_{43} \approx -13.31$$
$$(< -12.73),\ \log \beta_{64} \approx -20.59\ (< -19.40) \text{ etc. for 3 M (Na)ClO}_4 \text{ medium} \qquad (5)$$

This model requires only three parameters (β_{22}, β_{53}, k_0), and it is a philosophical question whether it should be preferred to other three-, four- or five-parameter models which give a slightly higher $\sigma(Z)$.

However, we will not take the improvement as a proof for an unlimited mechanism but as an indication that at least some of the $(2n, n + 1)$ complexes are present.

Finally, in set (6), we have introduced the (1,1) complex, which seems to give some improvement, and would give the log β values:

$$\log \beta_{22} = -6.07 \pm 0.02,\ \log \beta_{43} \approx -13.21\ (< 12.97),\ \log \beta_{53} = -16.53 \pm$$
$$0.03,\ \log \beta_{11} \approx -6.10\ (< -5.86). \qquad (6)$$

For discussion and acknowledgements, the reader is referred to the introductory paper, Part 46.[1]

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