

## Equilibrium Studies of Polyanions

### 7. The First Step in the Acidification of $\text{WO}_4^{2-}$ ; Equilibria in 3 M $\text{NaClO}_4$ at 25° C

YUKIYOSHI SASAKI

*Department of Inorganic Chemistry, The Royal Institute of Technology, Stockholm 70, Sweden*

The reaction between  $\text{H}^+$  and the wolframate ion,  $\text{WO}_4^{2-}$ , has been studied at 25°C in 3 M  $\text{NaClO}_4$  medium using a glass electrode. The main reaction was found to be:  $7 \text{H}^+ + 6 \text{WO}_4^{2-} \rightleftharpoons 3 \text{H}_2\text{O} + \text{HW}_6\text{O}_{21}^{5-}$  with the equilibrium constant  $\log K = 60.68 \pm 0.03$ . On further acidification, a range with slow reactions was encountered. The product  $\text{HW}_6\text{O}_{21}^{5-}$ , which is probably identical with the "parawolframate A" of Souhay and others, undergoes a slow reaction which does not seem however to affect the present data.

It is well known that isopolyanions are formed when acid is added to a wolframate solution, and that polywolframate salts may be crystallized from the solution.

*The crystal structures.* The crystal structure for the sodium "parawolframate",  $\text{Na}_{10}\text{W}_{12}\text{O}_{41}(\text{H}_2\text{O})_{28}$ , has been subjected to an X-ray investigation by Lindqvist<sup>1</sup> who found that it contains separate groups  $\text{W}_{12}\text{O}_{46}^{9-}$ . Keggin<sup>2</sup> pointed out the apparent isomorphism (powder photographs) of the "metawolframate",  $\text{K}_4\text{H}_4\text{W}_{12}\text{O}_{40}(\text{H}_2\text{O})_{18}$ , and the wolframosilicate,  $\text{K}_4\text{SiW}_{12}\text{O}_{40}(\text{H}_2\text{O})_{18}$ . Since, according to him, the latter salt contains discrete groups  $\text{SiW}_{12}\text{O}_{40}^{4-}$ , he concluded that the metawolframate contains groups  $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$ . This view has been supported by preparative work of Schott and Harzdorf<sup>3</sup>.

*Work on solutions.* Wolframate solutions of  $\text{pH} > 10$  contain the mononuclear species  $\text{WO}_4^{2-}$ , as has been proved repeatedly, for instance by spectrophotometric<sup>7</sup> and cryoscopic<sup>12</sup> work. The wolframate ion,  $\text{WO}_4^{2-}$ , has also been found in several crystal structures<sup>4-6</sup>.

Jander and his coworkers<sup>7-9</sup> concluded, mainly from their measurements of diffusion coefficients, that the dominant complex between  $\text{pH} = 8$  and  $\text{pH} = 6$  is  $\text{HW}_6\text{O}_{21}^{5-}$ . Further addition of acid leads to the formation of  $\text{H}_3\text{W}_6\text{O}_{21}^{3-}$  and, in concentrated solutions, a more condensed anion,  $\text{H}_6\text{W}_{12}\text{O}_{40}^{6-}$ , is also formed<sup>10,11</sup>.

Later on, Souchay<sup>12</sup> studied the wolframate ions by potentiometric, cryoscopic, and polarographic methods. His conclusion was that there are two "parawolframate" of the same formula,  $\text{HW}_6\text{O}_{21}^{5-}$ . "Parawolframate A" is slowly transformed into an ion, "parawolframate B", which differs from "A" in some reactions. For example, A but not B forms wolframosilicate with silicate anions. If more acid is added, parawolframate A yields " $\psi$ -metawolframate",  $\text{H}_3\text{W}_6\text{O}_{21}^{3-}$ , whereas B does not seem to react with  $\text{H}^+$ .

If a solution of  $\psi$ -metawolframate is boiled, it is transformed into "metawolframate",  $\text{H}_6\text{W}_{12}\text{O}_{42}^{6-}$ . According to Souchay, this reaction does not occur at room temperature.

After some additional experiments, Jander and Krüerke<sup>13</sup> accepted Souchay's picture of the situation with the modification that, according to Jander, there are also two different anions with the formula  $\text{H}_3\text{W}_6\text{O}_{21}^{3-}$ , namely "metawolframate A" and " $\psi$ -metawolframate".

Another mononuclear species,  $\text{HWO}_4^-$ , was claimed by Jander and Krüerke<sup>13</sup> and recently by Schwarzenbach and Meier<sup>14</sup>. Ripan and co-workers<sup>15</sup>, from conductometric and emf work, also found support for the formulae  $\text{HW}_6\text{O}_{21}^{5-}$  and  $\text{H}_3\text{W}_6\text{O}_{21}^{3-}$ . Pan and Hseu<sup>17,18</sup> reported the existence of the complexes  $\text{W}_2\text{O}_7^{2-}$ ,  $\text{W}_3\text{O}_{11}^{4-}$ ,  $\text{HW}_6\text{O}_{21}^{5-}$ ,  $\text{H}_2\text{W}_6\text{O}_{24}^{4-}$ , and  $\text{H}_3\text{W}_6\text{O}_{27}^{3-}$ . Another set of complexes,  $\text{H}_3\text{W}_2\text{O}_9^{3-}$ ,  $\text{H}_4\text{W}_3\text{O}_{13}^{4-}$ ,  $\text{W}_3\text{O}_{13}^{8-}$ ,  $\text{H}_{10}\text{W}_{12}\text{O}_{46}^{10-}$ , and  $\text{H}_2\text{W}_{12}\text{O}_{46}^{6-}$ , were claimed by Freedman<sup>16</sup> who like Pan and Hseu mainly drew his conclusions from the bends on titration curves.

Bettinger and Tyree<sup>19</sup> concluded from light-scattering data, that a triwolframate ion predominates in the range between mono- and hexawolframates.

Spitsyn and Pirogova<sup>20,21</sup> used dialysis techniques to measure the molecular weight of the wolframate complexes present in solutions. They concluded that the general formula of the products obtained on acidification of a  $\text{Na}_2\text{WO}_4$  solution can be written  $(\text{HW}_6\text{O}_{21}^{5-}(\text{H}_2\text{O})_x)_n$ , where  $n = 1$  at  $\text{pH} = 6$  to 6.5, and  $n = 8$  at  $\text{pH} = 5.0$  to 5.8. In solutions prepared by dissolving parawolframate crystals, the molecular weight corresponded to  $\text{W}_{12}\text{O}_{41}^{10-}(\text{H}_2\text{O})_{28}$  before boiling the solution, and  $\text{HW}_6\text{O}_{21}^{5-}(\text{H}_2\text{O})_{13.5}$  after boiling. According to Spitsyn and Pirogova, solutions of metawolframate crystals contain complexes with molecular weights fifty times greater than that of  $\text{WO}_4^{2-}(\text{H}_2\text{O})_2$ .

The present work was started in order to study the wolframate ions by methods previously used in this Department for other systems. Considerable difficulties were met with due to slow attainment of equilibrium in certain pH and concentration ranges. However, enough data were obtained to study the equilibrium of the first reaction step at 25°C.

## SYMBOLS

The symbols used in this paper conform with few exceptions, to those in the papers "AB I" and "AB II" (Sillén<sup>23,24</sup>):

$B$  = total W concentration;  $b$  = concentration of  $\text{WO}_4^{2-}$ ;  $c_n$  = concentration of a complex with  $n$  links (10);  $E$  = measured emf in mV;  $E_o = E - E_1 - 59.15 \log h$  (1);  $E_1(h)$  = liquid junction potential as a function<sup>29</sup> of  $h$ ;  $E_{\text{qoh}} = E_o$  for the quinhydrone electrode;  $E_{\text{og}} = E_o$  for a glass electrode;

$F = B/b$  (11);  $g = \Sigma k_n u^n$  (12,15);  $H =$  total (analytical) excess concentration of  $H^+$  calculated assuming no reaction with  $WO_4^{2-}$ ;  $h = [H^+]$ ;  $\bar{h} =$  normalized variable, corresponding to  $h$ , defined by (22);  $k =$  constant defined by (20);  $K = k_5 = \beta_{76}$  equilibrium constant of (17);  $k_n = \beta_{in,n+1}$ ;  $n =$  number of "links" ( $H_iWO_4$ ) per complex;  $\bar{n} =$  average number of "links" per complex (10);  $p =$  number of  $H^+$  in complex;  $\bar{p} =$  average number of  $H^+$  per complex (excepting  $WO_4^{2-}$ ), (5);  $P =$  unique value of  $p$  (21);  $q =$  number of W per complex;  $\bar{q} =$  average number of W per complex (excepting  $WO_4^{2-}$ ), (6);  $Q =$  unique value of  $q$  (21);  $R =$  reciprocal of the average degree of condensation (3);  $t =$  number of  $H^+$  per "link" (7);  $u = bh^t$  (13, 14);  $x = t \log h + \log B$  (9);  $y = Z/t$  (8);  $Z =$  average number of  $H^+$  bound per  $WO_4^{2-}$  (7);  $z = Z - 2 =$  average charge per W;  $\beta_{pq} =$  equilibrium constant of the reaction  $pH^+ + qWO_4^{2-} \rightleftharpoons H_pW_qO_{4q}^{p-2q*}$ .

## EXPERIMENTAL

### Methods

As in studies on other systems, the aim was to obtain data  $Z(\log h)_B$  (see list of symbols) in a wide range and to use them to calculate the formulas and formation constants of the species present.

In order to keep the activity factors of the wolframates and other anionic species as constant as possible during the acidification,  $[Na^+]$  was kept at 3 M in all solutions by adding  $NaClO_4$ .

Glass electrodes were used in all measurements of  $[H^+] = h$  because preliminary experiments had shown that, in part of the range we had to cover, the solutions were too alkaline for the use of a quinhydrone electrode and also because the hydrogen electrode is reported to reduce wolframate solutions<sup>22</sup>.

Most of the experiments were carried out as "titrations", *i.e.* by adding perchloric acid to the  $Na_2WO_4$  solution at  $25 \pm 0.1^\circ C$  and keeping  $B$ , the total concentration of W, constant by adding an appropriate amount of  $Na_2WO_4$  solution from another buret. Reverse titrations were also performed. Wolframate concentrations from 0.0012 M to 0.16 M were used in eight independent titrations. Some spectrophotometric measurements were made at  $25^\circ C$  and with the same ionic medium in order to construct the extinction curves for the species present.

### Chemicals and apparatus

*Sodium perchlorate* was prepared from  $Na_2CO_3$  (Merck p.a.) and  $HClO_4$  (Kebo p.a.) as described previously<sup>26</sup>. After a recrystallization from water, it was kept as a  $\sim 5$  M solution in a Pyrex glass bottle. Possible impurities are Fe and Al. Any traces of these present were concentrated by extraction with oxine and chloroform and the absorption peaks of the oxine complexes of these elements were searched for using a Hilger Uvispec Spectrophotometer.

In a 5 M  $NaClO_4$  solution which had been kept in a Pyrex bottle for about two months, the amount of Al found corresponded to 0.003 mM Al in 3 M  $NaClO_4$  solution. No definite evidence for Fe was found and, from the sensitivity of the method, it was calculated that there was at most 0.0003 mM Fe in 3 M  $NaClO_4$ . No  $Cl^-$  or  $SO_4^{2-}$  could be detected with  $AgNO_3$  and  $BaCl_2$ .

\* In this paper,  $WO_4^{2-}$  is treated as the central group and  $H^+$  as the ligand. If, instead,  $WO_4^{2-}$  is considered as the ligand (*i.e.* in the IUPAC Tables of Stability constants<sup>25</sup>), the order of the subscripts should be reversed:  $K$  for (17) is  $\beta_{67}$ , instead of  $\beta_{76}$  etc.

*Sodium wolframate* (Merck p.a.) was recrystallized twice from water under a stream of nitrogen. In this way, a certain impurity (probably Al and Fe) was removed which precipitates from solutions of the commercial reagent on the addition of NaOH. The purified product was heated to *ca.* 150°C, after which it was dissolved in twice-distilled water and freed from carbon dioxide at room temperature using nitrogen. The solution was filtered through a glass filter G 4 and diluted to give a stock solution with *ca.* 1.5 mole W/kg solution. The stock solution was kept in a polythene bottle.

In the solution thus prepared, no Tyndall effect could be detected even when a strong light beam was used. On the other hand, solutions of commercial sodium wolframate gave a strong Tyndall effect even after long boiling.

*Analysis:* A known amount of solution was evaporated and dried in an oven at 150°C overnight. Weighing the residue as  $\text{Na}_2\text{WO}_4$  gave quite reproducible results. To determine the concentration of  $\text{Na}^+$ , a known amount of stock solution was diluted and passed through a column of  $\text{OH}^-$ -saturated anion exchanger Dowex-2 and the  $\text{OH}^-$  set free was titrated potentiometrically with acid<sup>27</sup>. The reliability of the method was tested using  $\text{Na}_2\text{SO}_4$ .

The values for  $[\text{Na}^+]$  obtained by ion exchange and by weighing agreed within less than 0.1 %.

A few hours before each experiment the wolframate solutions for the equilibrium "titrations" were prepared from measured quantities of the stock solutions of  $\text{Na}_2\text{WO}_4$  and  $\text{NaClO}_4$ . Both solutions were first diluted separately with boiled distilled water and then mixed in a measuring flask. Otherwise, when concentrated solutions of  $\text{Na}_2\text{WO}_4$  and  $\text{NaClO}_4$  are mixed, a white precipitate occurs which does not dissolve on dilution or shaking.

*Perchloric acid, sodium hydroxide and silver perchlorate* were prepared and standardized as described previously<sup>24</sup>. The Ag, AgCl electrodes were made by Brown's method<sup>28</sup>.

Radiometer Red glass electrodes (Copenhagen, type 202 B) were used throughout all the work. The electrodes were tested against a quinhydrone electrode in a phosphate solution containing 3 M  $\text{Na}^+$  to which acid was gradually added. The potential difference between the glass and quinhydrone electrodes remained constant to within 0.1 mV throughout the pH range used, from 2 to 7.1. (See also "Determination of *h*" below.)

The emf was read to 0.1 mV by means of a Radiometer PHM3i valve potentiometer.

The "titration vessel" containing the equilibrium mixture was kept in an oil thermostat at  $25 \pm 0.1^\circ\text{C}$  placed in a room thermostated at  $25^\circ\text{C}$ .

## PROCEDURE

The cell may be written as follows:

glass electrode/solution//SE

where the reference half-cell is

$\text{SE} = 3 \text{ M NaClO}_4 // 2.990 \text{ M NaClO}_4, 0.010 \text{ M AgClO}_4 / \text{AgCl}, \text{Ag}$

At the beginning of each titration, the solution in the vessel had the composition 3 M  $\text{Na}^+$ , *B* M  $\text{WO}_4^{2-}$  and  $(3 - 2B)$  M  $\text{ClO}_4^-$ . To this solution, equal volumes were added from two burets, one containing  $\text{HClO}_4$  and 3 M  $\text{NaClO}_4$  and the other  $2B$  M  $\text{WO}_4^{2-}$ , 3 M  $\text{Na}^+$  and  $(3 - 4B)$  M  $\text{ClO}_4^-$ . In this way, the total wolframate content, *B*, was kept constant throughout the titration.

Nitrogen gas was bubbled continuously through the solution to keep out  $\text{CO}_2$  and, after each addition of acid, the solution was shaken to prevent any local excess of acid.

## Determination of *h*

From the measured *E*,  $h = [\text{H}^+]$  is calculated<sup>39</sup> from

$$E = E_o + E_j(h) + 59.15 \log h \quad (1)$$

In the present study, the liquid-junction potential  $E_j$  was negligible because always  $h < 10^{-3}$  M.

In our preliminary experiments, the constant  $E_0$  was determined in an independent "titration" in the same medium, 3 M  $\text{Na}(\text{ClO}_4)$ , in which acid was added in the absence of wolframate. However, we soon found that, for most of our glass electrodes, the values for  $E_0$  measured before and after a wolframate titration disagreed. Sometimes a discrepancy of 2 mV was met with. This may be connected with the large jump in pH between the  $\text{Na}_2\text{WO}_4$  solution with pH about 8 and the acidic solution with  $h \sim 0.1$  M in which the value for  $E_0$  was determined. Some preliminary attempts were made to calibrate the glass electrode by using it, instead, in alkaline solutions of known  $[\text{OH}^-]$ , with or without wolframate present, but these were abandoned when a better calibration method was found.

In the following, the  $E_0$  for the glass electrode was determined by measuring its potential in a phosphate solution 3 M in  $\text{Na}(\text{ClO}_4)$  and with  $h$  close to that of the wolframate solutions studied. This reference solution was prepared by mixing solutions of  $\text{Na}_3\text{PO}_4$ ,  $\text{HClO}_4$  and  $\text{NaClO}_4$ . The hydrogen ion concentration in this solution,  $h$ , was determined accurately by means of a quinhydrone electrode (using a Leeds and Northrup compensator, type K). The standard potential,  $E_{\text{qnh}}$ , of the quinhydrone electrode had been determined earlier by means of an acidic solution of known  $h$ .

Thus, we knew for the phosphate buffer,  $E_{\text{qh}} - E_{\text{qnh}} = 59.15 \log h$ , with an accuracy of 0.03 mV, and the  $E_0$  for the glass electrode was calculated from  $E_{\text{og}} = E_{\text{g}} - E_{\text{qh}} + E_{\text{qnh}}$ . In the "titrations" given here,  $E_{\text{og}}$  determined in this way before and after the main titration differed by at most  $\pm 0.2$  mV.

Knowing  $E_{\text{og}}$ ,  $h$  could be calculated for each solution using (1). Since, from the analytical composition of the solutions, we knew  $B$  (the total W concentration) and  $H$  (the analytical  $\text{H}^+$  excess), we could easily calculate  $Z$ , (the average number of  $\text{H}^+$  bound per  $\text{WO}_4^{2-}$ ), by means of the equation

$$H - h = BZ \quad (2)$$

### Equilibration

Whereas solutions with  $Z < 1.15$  seem in general to give reversible equilibria, irreversible phenomena and slow reactions were met with at higher values for  $Z$ . It thus seems convenient to discuss first of all the range  $Z < 1.15$  and thereafter higher  $Z$  values.

For  $Z < 1.15$ , and especially at the lowest values for  $Z$ , it appears that the equilibrium was established quickly since stable potentials were obtained almost instantaneously. In the solutions with the highest  $B$  values, a white precipitate was observed immediately after the addition of acid but it dissolved quickly on vigorous shaking. At the three highest concentrations used,  $B = 0.040$ ,  $0.080$ , and  $0.160$  M, the dissolution of the precipitate was slower already at  $Z \sim 0.7$  to  $1.0$ , and the solution began to show a strong Tyndall effect. Even if the emf seemed to have settled within some 10 minutes (in the other solutions for  $Z < 1.15$ , the emf became constant practically immediately) these solutions may not correspond to true equilibrium. In Fig. 1, which

contains the data obtained, the theoretical curves are dotted within this "colloidal" region.

To test the reversibility, two reverse titrations were performed, both at  $B = 0.020$  M, in which an alkaline solution was added to a solution with  $Z \sim 1.10$ . As seen from Fig. 1, the points fall on the same curve for increasing and decreasing  $Z$ . On the other hand, starting from a value for  $Z > 1.15$ , the titration curves with decreasing and increasing  $Z$  did not coincide.

The region  $Z > 1.15$ , may be described as an "instability range", analogous to those found in the silicate<sup>30</sup> and vanadate<sup>31,32</sup> systems.

In a titration with increasing  $Z$  the emf was found, at a point with  $Z > 1.15$ , to drift slowly for several days without reaching a stationary value. The drift is in the direction of decreasing  $h$  ( $Z$  increasing, but very little).

In two parallel experiments, the titrations with acid described above were continued to  $Z = 1.35$ . In one case, we had  $B = 0.04$  M. In the other, the original value of  $B$  was 0.08 M; the solution was then diluted with an equal amount of 3 M  $\text{NaClO}_4$  to give a solution which should have had, like the previous one,  $B = 0.04$  M and  $Z = 1.35$ . However, the emfs observed with the two solutions and hence their  $h$  values differed considerably. Even after two weeks, the difference was about 10 mV. These experiments indicated that the equilibration is very slow, and it did not therefore seem advisable to keep solutions of known  $Z$  in glass bottles for a long time in order to obtain equilibrium ("point titration"). It was thus decided that if equilibria were to be obtained in this range, it would be necessary to work at higher temperatures.

## RESULTS

The experimental data are given in Fig. 1 and in Table 1 in the form  $Z$  ( $\log h$ )<sub>B</sub>. Obviously, the points for different  $B$  values fall on different curves,

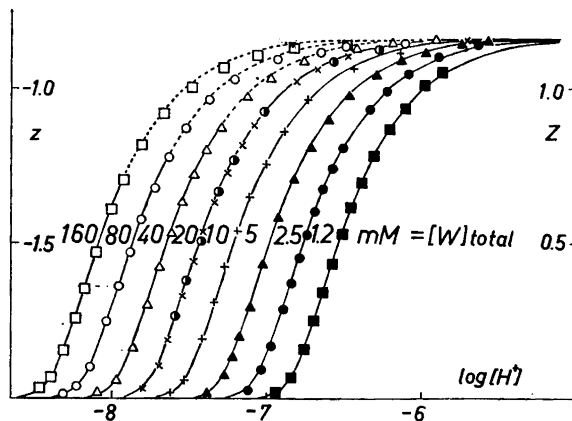


Fig. 1.  $z$  (average charge per W) and  $Z$  (number of protons bound per  $\text{WO}_4^{2-}$ ) as functions of  $\log [\text{H}^+]$ . The half-filled symbols for  $B = 20$  mM represent data obtained by a reverse titration. The lines are calculated curves for the reaction (17) and  $\log K = 60.67$ .

Table 1. Wolframate acidification at 25°C in 3 M Na(ClO<sub>4</sub>). Data  $Z(\log h)_B$  obtained with glass electrode.

$B = 0.00125 M. Z - \log h:$							
0.069,	6.852;	0.108,	6.809;	0.157,	6.769;	0.204,	6.735;
0.298,	6.676;	0.345,	6.647;	0.390,	6.615;	0.435,	6.586;
0.524,	6.524;	0.567,	6.495;	0.610,	6.464;	0.653,	6.427;
0.736,	6.360;	0.778,	6.316;	0.818,	6.275;	0.870,	6.209;
0.938,	6.111;	0.979,	6.038;	1.010,	5.979;	1.040,	5.910;
1.086,	5.780;	1.100,	5.726;	1.116,	5.666;	1.130,	5.606;
1.159,	5.469;	1.174,	5.382.				
$B = 0.0025 M. Z, - \log h:$							
0.094,	7.044;	0.108,	7.029;	0.126,	7.012;	0.172,	6.980;
0.254,	6.924;	0.288,	6.901;	0.331,	6.875;	0.373,	6.848;
0.531,	6.747;	0.605,	6.693;	0.676,	6.633;	0.744,	6.571;
0.873,	6.427;	0.935,	6.336;	0.993,	6.226;	1.048,	6.082;
1.123,	5.775;	1.144,	5.634;	1.154,	5.548;	1.164,	5.450;
$B = 0.0050 M. Z, - \log h:$							
0.055,	7.313;	0.074,	7.286;	0.105,	7.256;	0.134,	7.232;
0.201,	7.188;	0.245,	7.151;	0.294,	7.115;	0.342,	7.088;
0.510,	6.985;	0.582,	6.931;	0.647,	6.879;	0.706,	6.828;
0.809,	6.720;	0.856,	6.664;	0.899,	6.601;	0.939,	6.540;
1.010,	6.388;	1.041,	6.297;	1.058,	6.246;	1.073,	6.182;
1.115,	5.972;	1.128,	5.866;	1.141,	5.741;	1.153,	5.572;
$B = 0.0100 M. Z, - \log h:$							
0.059,	7.538;	0.083,	7.509;	0.108,	7.486;	0.132,	7.465;
0.252,	7.377;	0.311,	7.342;	0.369,	7.308;	0.426,	7.273;
0.539,	7.191;	0.594,	7.147;	0.649,	7.117;	0.703,	7.065;
0.808,	6.960;	0.861,	6.887;	0.913,	6.818;	0.964,	6.730;
1.066,	6.436;	1.116,	6.130;	1.135,	5.956;	1.160,	5.602.
$B = 0.0200 M. Z, - \log h:$							
0.034,	7.802;	0.046,	7.776;	0.059,	7.758;	0.083,	7.729;
0.160,	7.660;	0.189,	7.639;	0.218,	7.619;	0.274,	7.584;
0.383,	7.514;	0.441,	7.474;	0.488,	7.448;	0.538,	7.411;
0.635,	7.338;	0.683,	7.303;	0.729,	7.256;	0.774,	7.210;
0.861,	7.110;	0.883,	7.083;	0.904,	7.049;	0.945,	6.983;
1.025,	6.801;	1.064,	6.670;	1.084,	6.586;	1.099,	6.500;
1.114,	6.415;	1.121,	6.331;	1.129,	6.226;	1.151,	5.903;
1.160,	5.404;	— — —	1.129,	6.273*;	1.089,	6.569*;	1.045,
0.931,	7.019*;	0.771,	7.218*;	0.668,	7.318*;	0.511,	7.433*;
0.271,	7.607*;					0.382,	7.528*;
$B = 0.0399 M. Z, - \log h:$							
0.058,	7.979;	0.074,	7.956;	0.090,	7.940;	0.105,	7.923;
0.165,	7.874;	0.194,	7.852;	0.232,	7.824;	0.269,	7.802;
0.365,	7.741;	0.424,	7.702;	0.480,	7.666;	0.533,	7.628;
0.632,	7.555;	0.678,	7.516;	0.722,	7.475;	0.761,	7.437;
0.838,	7.349;	0.871,	7.301;	0.909,	7.249;	0.974,	7.131;
1.034,	6.980;	1.063,	6.887;	1.090,	6.760;	1.129,	6.426;
1.157,	5.908.					1.147,	6.189;

\* An asterisk indicates data from a reverse titration.

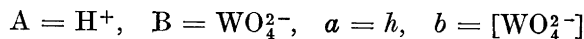
$B = 0.0797 M. Z, -\log h:$				0.016,	8.321;	0.022,	8.295;	0.028,	8.270;
0.034,	8.253;	0.041,	8.234;	0.071,	8.189;	0.087,	8.169;	0.102,	8.153;
0.132,	8.126;	0.162,	8.101;	0.192,	8.077;	0.250,	8.042;	0.307,	8.001;
0.364,	7.966;	0.419,	7.930;	0.473,	7.891;	0.526,	7.856;	0.578,	7.817;
0.635,	7.776;	0.680,	7.732;	0.732,	7.688;	0.778,	7.643;	0.873,	7.526;
0.965,	7.374;	1.009,	7.267;	1.031,	7.210;	1.053,	7.137;	1.074,	7.043;
1.096,	6.933;	1.117,	6.647;	1.138,	6.490;	1.150,	6.103.		
$B = 0.1604 M. Z, -\log h:$				0.014,	8.571;	0.025,	8.500;	0.033,	8.471;
0.040,	8.453;	0.055,	8.426;	0.071,	8.402;	0.100,	8.371;	0.129,	8.343;
0.158,	8.319;	0.193,	8.294;	0.227,	8.268;	0.260,	8.246;	0.292,	8.226;
0.355,	8.185;	0.386,	8.167;	0.415,	8.147;	0.473,	8.108;	0.529,	8.069;
0.556,	8.049;	0.582,	8.030;	0.608,	8.011;	0.633,	7.991;	0.675,	7.949;
0.705,	7.927;	0.775,	7.861;	0.818,	7.812;	0.921,	7.670;	1.007,	7.487;
1.042,	7.381;	1.069,	7.281;	1.082,	7.217;	1.109,	7.061;	1.122,	6.928;
1.132,	6.825;	1.141,	6.578;	1.148,	6.475;	1.160,	5.511.		

thus showing that polynuclear complexes are formed. Moreover, the curves seem to be practically parallel.

Two different approaches were made in order to find out the main reaction and the equilibrium constant involved. In the "integration method" no further assumption was made about the system apart from those that the activity factors can be considered constant and that the law of mass action is obeyed. In the "core and links" approach, it was assumed that the curves are exactly parallel as they seem to be.

### "Integration method"

An integration method has been developed by Sillén<sup>33</sup> which makes it possible to compute the average composition of the complexes from  $Z(\log h)_B$  data without any special assumption being necessary provided that equilibrium data of sufficient accuracy are available over a sufficient concentration range. In the present case the reagents are



and we have data from  $\log h \sim -8.5$  upwards. Using the equations given in Ref.<sup>33</sup> (see also Refs.<sup>32,34</sup>) we have for  $R$  (the average number of free molecules per  $W =$  the reciprocal value of the average number of  $W$  per  $W$  complex) and  $b = [WO_4^{2-}]$ :

$$R = 1 + \int_0^Z \left( \frac{\partial \log h}{\partial \log B} \right)_Z dZ \quad (3)$$

$$\log b = \log B + R - 1 - \int_{-8.5}^{\log h} Z d \log h \quad (4)$$

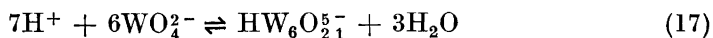


Because of the steepness of the curves, there is no need to consider the residual integral beyond  $-8.5$ .

Now, we may subtract  $b$  from  $B$  (the total concentration of W) and from  $BR$  (the total molecular concentration of W complexes), and thus calculate  $\bar{p}$  and  $\bar{q}$  which give the average number of  $H^+$  and  $WO_4^{2-}$  per complex in all W-complexes except  $WO_4^{2-}$ :

$$\bar{p} = \frac{BZ}{BR - b} \quad (5) \quad \bar{q} = \frac{B-b}{BR - b} \quad (6)$$

Table 2 gives the result of an numerical integration of  $Z(\log h)_B$  for  $B = 0.02$  M. It is seen that  $\bar{p} \sim 7$  to 8 and  $\bar{q} \sim 6$  to 7. Both values are rather constant which indicates that one polynuclear complex predominates among the reaction products. With  $p = 7$  and  $q = 6$ , the main reaction would be



if the complex is written with as little water as possible. However, this first survey would also leave the reaction products,  $W_6O_{20}^{4-}$ ,  $W_7O_{24}^{6-}$ , and  $HW_7O_{25}^{7-}$ , as possibilities to be further investigated.

#### "Core and links" approach

If the curves  $Z(\log h)_B$  are exactly parallel, with a constant spacing, this would indicate that all complexes present in appreciable amounts have the general formula  $B(A_nB)_n$  where

$$t = - \left( \frac{\partial \log B}{\partial \log h} \right)_Z \quad (7)$$

is a constant and  $n$  may have one or several values (Sillén<sup>23,24</sup>).

By measuring the spacing between the experimental curves (Fig. 1), we found  $t = 1.40 \pm 0.03$ .

In the following analysis of the data, we shall follow the methods and notations of ABII<sup>24</sup>. Fig. 2 gives

$$y = Z/t = Z/1.4 \quad (8)$$

Table 2. Analysis of the  $Z(\log h)$  for  $B = 0.02$  M

$Z$	$R$	$\frac{b}{\bar{B}}$	$\bar{p}$	$\bar{q}$
0.075	0.946	0.937	8.52	7.13
0.125	0.910	0.894	7.91	6.68
0.175	0.874	0.853	8.33	6.98
0.225	0.838	0.809	7.73	6.54
0.275	0.802	0.767	7.79	6.59
0.325	0.766	0.722	7.35	6.28
0.375	0.731	0.681	7.50	6.45
0.425	0.695	0.638	7.40	6.30
0.475	0.659	0.596	7.55	6.40
0.525	0.623	0.555	7.63	6.46
0.575	0.588	0.509	7.27	6.21
0.625	0.552	0.468	8.41	7.16

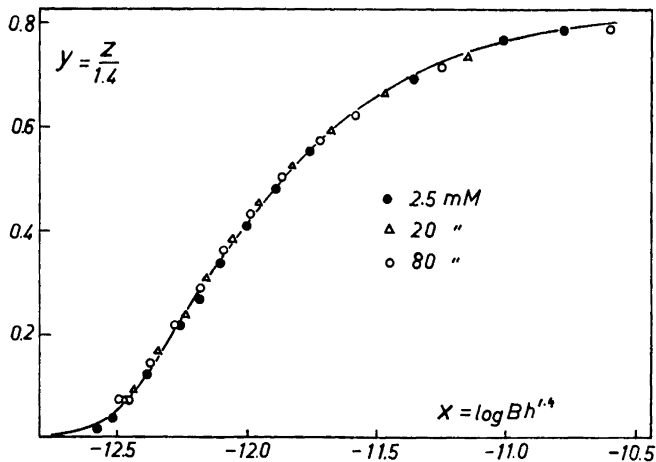


Fig. 2.  $y = z/1.4$  as a function of  $x = \log Bh^{1.4}$ . The curve is calculated from eqns. (22) and (23) in ABII for  $N = 5$  and  $\log K = 60.70$ .

as a function of

$$x = \log B + t \log h = \log B + 1.4 \log h \quad (9)$$

All of the experimental points in this diagram fall on a single curve within the experimental accuracy, as required if  $t$  in (7) is constant.

To find the value, or values, of  $n$ , one may either carry out a "direct analysis" of the function  $y(x)$  or compare it with a group of theoretical curves.

*Direct analysis.* From the relationship between  $B$ ,  $b$ ,  $t$  and  $Z$ , it can be shown that

$$\bar{n} = \frac{y}{1 - y - bB^{-1}} \quad (10)$$

(viz.  $BZ = t \sum n c_n$ ;  $B = b + \sum (n+1)c_n$ ;  $\bar{n} \sum c_n = \sum n c_n$ ;  $Z = ty$ )

Table 3. Direct analysis of  $y(x)$

$y$	$F^{-1}$	$\bar{n}$	$\log u$	$\log g$	$\log K_s$
0.025	0.972	8.62	-12.57	-2.525	60.33
0.050	0.942	6.49	-12.51	-2.087	60.46
0.075	0.913	6.75	-12.49	-1.915	60.54
0.10	0.884	6.28	-12.46	-1.745	60.56
0.15	0.824	5.79	-12.43	-1.502	60.65
0.20	0.762	5.30	-12.38	-1.305	60.60
0.25	0.701	5.10	-12.36	-1.155	60.65
0.30	0.639	4.98	-12.35	-1.026	60.73
0.35	0.579	4.98	-12.32	-0.917	60.69
0.40	0.520	5.02	-12.30	-0.814	60.69
0.45	0.458	4.93	-12.28	-0.702	60.70
0.50	0.397	4.88	-12.26	-0.589	60.71
0.55	0.339	5.42	-12.24	-0.487	60.72
0.60	0.280	5.03	-12.21	-0.372	60.68

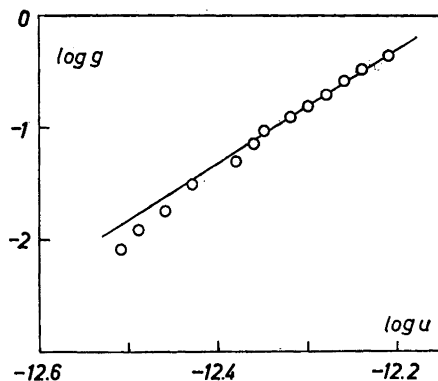


Fig. 3. Direct analysis of the curve  $y(x)$  in Fig. 2,  $\log g$  as a function of  $\log u$ . A straight line with slope 5 is shown at the position of best fit.

Here,  $\bar{n}$  is the average number of links  $H_{1.4}WO_4$  per complex, and  $bB^{-1}$ , which cannot be measured directly, can be calculated from the curve  $y(x)$  by means of the formula (derived from ABII<sup>24</sup>, eqns. 14, 8a and 5a).

$$\log F = \log Bb^{-1} = y \log e + \int_{-\infty}^x y dx \quad (11)$$

From smoothed curves through the points  $(x, y)$ , the values of  $\bar{n}$  given in Table 3 were obtained. If the first less accurate values are excluded, the table indicates a constant value  $\bar{n} = N = 5$  so there is no need to assume higher complexes in any appreciable amount.

The same conclusion and also the same equilibrium constant are obtained from another type of diagram (Fig. 3).  $\log g$  has been plotted as a function of  $\log u$  where  $g$  and  $u$  were calculated from:

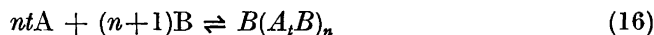
$$g = F(1 - y) - 1 \quad (12)$$

$$u = 10^x F^{-1} \quad (13)$$

using the experimental values for  $x$  and  $y$  and also the  $F$  calculated by means of (11). As shown in AB II<sup>24</sup> (eqns. 5a, 14 and 15), provided the "core and links" complexes predominate,  $u$  and  $g$  calculated in this way are the quantities:

$$u = bh^t \quad (14); \quad g = \sum k_n u^n \quad (15)$$

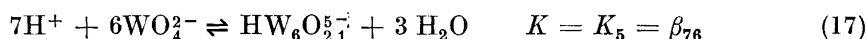
Here,  $k_n$  is the equilibrium constant for the reaction



In our case, we remember that  $A = H^+$ ,  $B = WO_4^{2-}$ , and  $t \sim 1.40 \pm 0.03$ . As seen from Fig. 3, the slope agrees well with the theoretical one for  $n = 5$ . The points in the lower left corner of the diagram are those most sensitive

to experimental error. At any rate, the slope corresponding to  $n = 6$  would not fit the data at all. Besides with  $n = 6$  the formula of the complex would not contain an integral number of atoms. With  $n = 5$  and  $t = 1.4$ , the formula of the complex is  $H_7W_6O_{24}^{5-}$  or  $HW_6O_{21}^{5-}$ . We shall use the second formula; if nothing is known about the structure of a complex it is often preferred to write it with as little water as possible.

The main reaction is thus



The other possible reaction products suggested by the "integration method",  $W_6O_{20}^{4-}$ ,  $W_7O_{24}^{6-}$ , and  $HW_7O_{25}^{7-}$ , were definitely ruled out, since they give  $t$  values of 1.6, 1.33 and 1.17, respectively. Such values would give a spacing between the curves different from that observed.

Since from (15),  $g = K_5u^5$  we may find the equilibrium constant for reaction (17) either from the intercepts of  $\log g(\log u)$  or numerically, using for instance the equation

$$\log K = \log g - 5x + 5 \log F \quad (19)$$

The results of numerical calculations with (19) are given in Table 3. There is no trend in the values except for the very first ones and the average is

$$\log K = 60.68 \pm 0.03$$

(The first three points were excluded when calculating the average.)

From the graph, the value for  $\log K$  was found to be:

$$\log K = 60.69 \pm 0.02$$

Fig. 1 shows theoretical curves  $Z(-\log h)_B$  calculated for the reaction and the constant thus obtained. The agreement with the experimental points is satisfactory.

### Curve fitting

The experimental curve  $y(x)$  was also compared with various families of theoretical curves calculated for various mechanisms (AB II)<sup>24</sup>. It was found to fit very well with the curve calculated by assuming only one complex with  $n = N = 5$  which supports the previous results. From the position of best fit, we may calculate  $K = k^5$  using (AB II)<sup>24</sup>, eqn. 24):

$$x_{\frac{1}{2}} = \log 2 - \log k + \log N - (1 + N^{-1}) \log (N - 1) \quad (20)$$

The result was  $\log K = 60.70 \pm 0.05$

Another type of curve-fitting was tried, once the formula of the complex was established, by constructing  $Z(\log h)_B$  curves. We start from eliminating  $b$

$$B = b + QKb^q h^P \quad (21a); \quad BZ = PKb^q h^P \quad (21b)$$

$P = tN$  and  $Q = 1 + N$  are the values for  $p$  and  $q$  in the complex in the present case,  $P = 7$ ,  $Q = 6$ . We may introduce a normalized function  $h$  making

$$7(\log h - \log h) = \log K + 5 \log B - \log 7 \quad (22)$$

Elimination of  $b$  and  $h$  from (21) and (22) then gives

$$7 \log h = \log Z - 6 \log (1 - 6 Z 7^{-1}) \quad (23)$$

One may construct a diagram  $Z(\log h)$  using eqn. (23) and compare this curve with each separate curve  $Z(\log h)_B$ . From the value of best fit, one finds  $(\log h - \log h)$  and thus, using (22),  $\log K$ . The average value found was  $\log K = 60.67 \pm 0.05$ .

There was no trend among the different  $B$  values which also supports our conclusion that the main reaction is (17).

#### SPECTROPHOTOMETRIC EXPERIMENTS

Knowing what the main reaction was, we intended to construct the extinction curve for the anion,  $\text{HW}_6\text{O}_{21}^{5-}$ , by measuring absorption spectra of wolframate solutions with different values for  $Z$  and  $B$ . However, we soon found that the extinction coefficient drifted with time and that Beer's law is valid only in freshly mixed solutions or solutions which contain excess  $\text{NaOH}$ . In the course of a few hours or a day, a new species was apparently formed with a much stronger absorption in the range 2 500 — 3 250 Å. This species may be identical with the "parawolframate B" of Souchay whereas the ions formed immediately on equilibrium would be identical with his "parawolframate A"<sup>12</sup>.

Whatever the nature of this slow reaction, it is so slow that it does not seem to influence the results of the emf studies described here, but, because of the strong absorption of the new species, it made the spectrophotometric work very difficult.

#### COMPARISON WITH PREVIOUS WORK

Our conclusion that the main complex is  $\text{HW}_6\text{O}_{21}^{5-}$  agrees with the results of Jander, Souchay and others quoted in the introduction. On the other hand, our results do not support the existence of the species with 2 or 3 W suggested by Freedman, Pan and Hseu and others. Nor do our data seem to support the existence of complexes with 12 W or more in freshly prepared solutions<sup>21</sup>. We have not been able to locate any earlier equilibrium constants for the wolframate-hexawolframate equilibrium.

A few words must be said about  $\text{HWO}_4^-$  and  $\text{H}_2\text{WO}_4$ . Schwarzenbach and Meier<sup>13</sup> mixed two streams of solutions containing, respectively, wolframate and acid, and placed a glass electrode immediately after the mixing point. Their data gave evidence for  $\text{HWO}_4^-$  and  $\text{H}_2\text{WO}_4$ , with the average equilibrium constant  $\frac{1}{2}\beta_{21} = 4.05$  (see footnote, page 177). It seems that, under these conditions, the polynuclear complex did not have time to form. By comparison with the present data, one finds that the mononuclear complexes would form an appreciable fraction of the total W only at much lower values for  $B$  (0.01 to 0.001 mM) than those practicable in the present work.

On the other hand, in the molybdate system, where the same emf methods were applied<sup>35</sup>, definite evidence was found indicating the existence of the mononuclear species  $\text{HMoO}_4^-$ .

*Future work.* It is planned to investigate the wolframate equilibria at higher temperatures with a new technique for emf-titration<sup>37</sup>. In this way, it is hoped to reach equilibrium within a reasonable time, which may thus throw more light on the mechanism of the slow reactions.

From wolframate solutions of  $\text{pH} \sim 5.2$ , a sodium "parawolframate"  $\text{Na}_{10}\text{W}_{12}\text{O}_{41}(\text{H}_2\text{O})_{28}$  crystallizes slowly<sup>36</sup>. Souchay for various reasons has concluded that this phase contains "parawolframate B" ions. According to a recent X-ray investigation by Lindqvist<sup>1</sup>, it contains discrete anions, with 12 W-atoms, whereas Souchay considers that the "parawolframate B" contains 6 W. This problem would be worth further investigation.

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