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Equilibrium Studies of Polyanions. 20. A Recalculation of emf Data on the Reactions of H^+ and WO_4^{2-} in 3 M $Na(ClO_4)$ at 25°C

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In 1961 one of us (Y.S.) published emf data on the reactions between H^+ and WO_4^{2-} in 3 M $Na(ClO_4)$ at 25°C.[1] Recently we have performed a new analysis of the data by means of the generalized least-squares computer program LETAGROP.[2,3] A large number of combinations of species $(H)_p(WO_4)_q^{(2q-p)-}$ have been tried in order to get the best fit with the data. We find that the emf data can best be explained by assuming the species H_2WO_4, $W_6O_{21}^{6-}$, and $W_{12}O_{41}^{10-}$ in addition to $HW_6O_{21}^{5-}$ with the equilibrium constants (deviations correspond to 3σ):

$$2H^+ + WO_4^{2-} \rightleftharpoons H_2WO_4$$
$$6H^+ + 6WO_4^{2-} \rightleftharpoons W_6O_{21}^{6-} + 3H_2O$$
$$7H^+ + 6WO_4^{2-} \rightleftharpoons HW_6O_{21}^{5-} + 3H_2O$$
$$14H^+ + 12WO_4^{2-} \rightleftharpoons W_{12}O_{41}^{10-} + 7H_2O$$

$$\log \beta_{2,1} = 11.30 \pm 0.10$$
$$\log \beta_{6,6} = 52.46 \pm 0.10$$
$$\log \beta_{7,6} = 60.76 \pm 0.03$$
$$\log \beta_{14,12} = 123.24 \pm 0.15$$

At this Institute in 1961 Sasaki[1] studied the reactions between H^+ and the wolframate ion WO_4^{2-} in 3 M $Na(ClO_4)$ medium at 25°C using a glass electrode. The main reaction was found to be

$$7H^+ + 6WO_4^{2-} \rightleftharpoons HW_6O_{21}^{5-} + 3H_2O$$

with the equilibrium constant $\log \beta_{7,6} = 60.68 \pm 0.03$

In connexion with a calorimetric study of the $H^+ - WO_4^{2-}$ system[4] it was found to be desirable to recalculate the emf data with the modern computer methods now available, and so we have used a recent version of the generalized least-squares computer program LETAGROP.

Various authors have proposed species $H_p(WO_4)_q^{(2q-p)-}$, with many different (p,q) values, in acidified wolframate solutions; for reviews see Refs.[5,6]

THE LETAGROP TREATMENT

The calculations were performed on the sets of data, $Z(\log h)_B$, given by Sasaki. The aim was to find a mechanism which gives a minimum to the error square sum defined

$$U = \sum (Z_{calc} - Z_{exp})^2$$

By means of LETAGROP it is possible to select, out of a number of suggested complexes, that set of complexes $(p,q,\beta_{p,q})$, which gives the lowest error square sum. Species which diminish the U-value and for which the condition $\beta_{pq} > F_\sigma\ \sigma(\beta_{pq})$ is fulfilled are accepted, others are rejected ("species selector").[7]

Many species, $H_p(WO_4)_q^{(2p-q)-}$, besides $HW_6O_{21}^{5-}$, have been suggested in literature,[5,6] among others the following: (p,q); (1,1), (2,1), (6,6), (8,6), (9,6), (12,12), (13,12), (14,12), (15,12), (16,12), (17,12), and (18,12).

We have now systematically tested these species with the "species selector" (the F_σ value used was 3). In this work we found rather soon that the combination of species (7,6), (6,6), and (14,12) gave a considerably lower U-value than the species (7,6) alone (Table 1, calc. I – III).

To the set (7,6) (6,6), and (14,12) we tried to add the other complexes suggested above, but all these complexes were ultimately rejected

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Table 1. log $\beta_{p,q}$, U and $\sigma(Z)$. $\delta Z = 0$.

(p,q)	I	II	III	IV	V
2,1	–	–	–	–	10.79 ± 0.08
6,6	–	–	52.46 ± 0.04	52.47 ± 0.04	52.48 ± 0.04
7,6	60.68 n.v.[a]	60.75 ± 0.01	60.71 ± 0.01	60.71 ± 0.01	60.70 ± 0.01
9,6	–	–	–	70.47 ± 0.07	–
14,12	–	123.17 ± 0.05	123.22 ± 0.05	123.23 ± 0.05	123.25 ± 0.05
U	0.157	0.050	0.031	0.027	0.028
$\sigma(Z)$	0.018	0.014	0.011	0.010	0.010

[a] Not varied

Table 2. log $\beta_{p,q}$, U and $\sigma(Z)$; adjusting for δZ.

(p,q)	I	II	III
2,1	11.30 ± 0.03	–	–
6,6	52.46 ± 0.03	52.56 ± 0.03	52.62 ± 0.03
7,6	60.76 ± 0.01	60.70 ± 0.01	60.64 ± 0.01
9,6	–	70.61 ± 0.05	–
14,12	123.24 ± 0.05	123.44 ± 0.04	123.52 ± 0.04
U	0.0082	0.0130	0.018
$\sigma(Z)$	0.0056	0.0071	0.0083

except (9,6). Initially the (2,1) species was accepted but it was subsequently rejected in favour of (9,6). However, σ_Z has the same value when (2,1) or (9,6) is accepted (Table 1, calc. IV and V).

In the above treatment, we have assumed no analytical errors, hence all $\delta Z = 0$. In a more complete treatment we assume a constant error in Z, δZ, for each "titration". These systematic errors are treated as unknown parameters to be adjusted together with the equilibrium constants.[8] This leads to the results given in Table 2 and Table 3. Starting with the (6,6), (7,6), (14,12), (9,6), and (2,1) set of species and adjusting the δZ, $\beta_{9,6}$ is found to be negative. If the (9,6) species is then left out (Table 2, calc. I), the value for $\sigma(Z)$ drops from 0.010 to 0.0056 with the δZ adjustment. Other sets of species give higher $\sigma(Z)$ with the δZ adjustment (Table 2, calc. II and III).

If the set of species (6,6), (7,6), (14,12), and (2,1) is assumed and taking the δZ in calc. I in Table 3, there remains no systematic deviation in the $(Z_{calc} - Z_{exp})$ values.

Table 3. Analytical errors $100 \times \delta Z$, calculated for various titrations by LETAGROP adjustment to best fit.

$W(VI)_{total}$,M	I	II	III
0.00125	−3.0 ± 0.4	−0.7 ± 0.5	0.4 ± 0.7
0.0025	−1.9 ± 0.3	−0.7 ± 0.3	0.4 ± 0.4
0.0050	−1.1 ± 0.2	−0.4 ± 0.2	0.2 ± 0.3
0.0100	0.3 ± 0.4	0.8 ± 0.6	1.4 ± 0.7
0.0200	0.2 ± 0.3	0.4 ± 0.4	0.7 ± 0.4
0.0399	−0.2 ± 0.2	−0.2 ± 0.2	−0.01 ± 0.2
0.0797	−0.3 ± 0.3	−0.5 ± 0.2	−0.5 ± 0.2
0.1604	−1.4 ± 0.3	−1.9 ± 0.4	−2.0 ± 0.4

In Fig. 1 are given the species fraction curves for $B = 0.1604$ M, calculated using the scheme with $HW_6O_{21}^{5-}$, $W_6O_{21}^{6-}$, $W_{12}O_{41}^{10-}$, and H_2WO_4. The fraction of the species H_2WO_4 for $[W(VI)]_{total} = 0.1604$ M is almost negligible, but amounts to about 10 % for $[W(VI)]_{total} = 0.00125$ M.

Slow formation of $W_{12}O_{41}^{10-}$ from $HW_6O_{21}^{5-}$ (ordinarily called parawolframate B and A, respectively) has been repeatedly reported.[9–12]

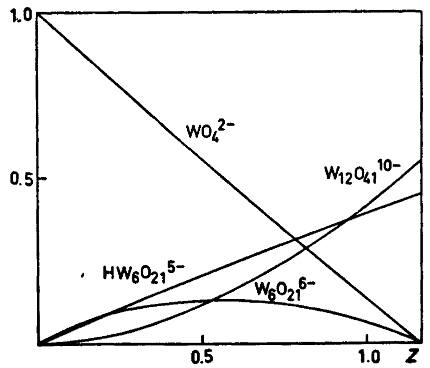

Fig. 1. Fractions of total W(VI) as WO_4^{2-}, $HW_6O_{21}^{5-}$, $W_6O_{21}^{6-}$ and $W_{12}O_{41}^{10-}$ in 3 M $Na(ClO_4)$ at 25° for 0.1604 M W(VI). Z = average number of H^+ bound per WO_4^{2-}. The fraction of H_2WO_4 is too small (< 0.004) as to appear in the figure.

In the present investigation, however, the establishment of equilibrium is found to be practically instantaneous, so the relationship between the anion $W_{12}O_{41}^{10-}$ found in the present study and "parawolframate B" is not yet clear.

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