Electrolytic Behavior of Elements of the Group VIa in the Periodic System.

I. Potentiometric Studies on the Chromate, Molybdate and Tungstate Ions

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Introduction

It has been known that molybdic and tungstic acids form well-defined soluble normal salts similar to those of chromates, but they do not resemble chromic acid in some electrolytic behaviors. In their abnormalities, however, molybdic and tungstic acids bear to one another remarkable similarities, such as the formation of poly-anions.

Several investigations on the formation of these poly-anions of molybdate and tungstate in aqueous solutions have been published since the beginning of the twentieth century.(1)~(8) These investigators suggested that, beside the normal ion MoO_4^{--}, various kinds of poly-anions may be formed in aqueous solution at varying dilutions and at different *p*H ranges. Thus the possible existence of $H_3Mo_6O_{21}^{3-}$, $HMo_6O_{21}^{5-}$, or $O(MoO_3)_n^{2-}$, has been proposed by estimating the ratio, Na_2O/MoO_3, from the experimental results of conductometric and potentiometric titrations of molybdate and tungstate with strong or weak acid. On account of the complexity of the relation of equilibria between these poly-anions, or due to the experimental difficulties, some of the conclusions seem to be overstrained or presumptive and further verifications seem to be left for the present investigation.

The present and subsequent papers in this

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(1) H. T. S. Britton and W. Leslie, *J. Chem. Soc.*, **1927**, 147.

(2) H. T. S. Britton and M. L. German, *J. Chem. Soc.*, **1930**, 1249; **1931**, 709.

(3) R. H. Vallance and E. G. K. Pritchett, *J. Chem. Soc.*, **1931**, 1421; **1934**, 1586.

(4) G. Jander, K. F. Jahr and W. Heukeshoven, *Zeit. anorg. allgem. Chem.*, **187**, 60, 129 (1930); **194**, 383 (1930).

(5) R. A. Robinson and D. A. Sinclair, *J. Chem. Soc.*, **1934**, 642.

(6) H. Brintzinger and C. Ratanarat, *Zeit. anorg. Chem.*, **224**, 97 (1935).

(7) E. Buchholtz, *Zeit. anorg. allgem. Chem.*, **244**, 149, 168 (1940).

(8) G. Carpeu, *Bull. soc. chim. France*, **1947**, 484, 490, 492.

series have attempted to verify the existence of these poly-anions from results obtained by means of potentiometric and conductometric measurements as well as by studies of the Raman spectra or absorption spectra of these solutions. The purpose of the present paper which reports the results of potentiometric measurements is three fold: first, to obtain more accurate data on the *p*H values of the aqueous solutions of molybdates and tungstates as well as chromates by means of a glass electrode and to ascertain the existence of dimolybdate and ditungstate ions, $X_2O_7^{--}$, from the *p*H changes governing the hydrolytic process of these salts; second, to verify the dissimilarities in electrolytic behavior between chromate and molybdate or tungstate by measuring the *p*H values at varying dilutions and checking the differential quotients, $dp\text{H}/d\log C$, which will also be expected from the theoretical calculation; third, to ascertain the existence of poly-anions at varying *p*H values by means of potentiometric titration of sodium molybdate or tungstate with hydrochloric acid.

Experimental

(1) **Materials.**—Conductivity water having a specific conductivity of 1.6 to 2.4×10^{-6} mho was prepared by refluxing and distilling water over potassium permanganate with sulfuric acid and then redistilling over barium hydroxide in pyrex glass apparatus.

Reagent grade hydrochloric acid was distilled twice. The constant boiling fraction was diluted to a desired concentration and used for the potentiometric titrations.

Reagent grade sodium molybdate and tungstate were recrystallized twice from the conductivity water and heated at 100°C. for two hours.

Potassium molybdate and tungstate were obtained by dissolving 1 mol. each of extra pure molybdic acid and tungstic acid, respectively, in a hot solution containing 2 mols. of potassium hydroxide. The salts separated on cooling were recrystallized, repeatedly, from the conductivity water and washed with 95% alcohol.

Sodium chromate and potassium chromate recrystallized twice from the conductivity water were used in this experiment.

The crystalline water as well as the composition of salts used in the present investigation was checked by the gravimetric method. The solutions were prepared, directly, by dissolving the salt in carbonate-free conductivity water and diluting to a desired concentration before each run.

(2) **Apparatus.**—A vacuum tube potentiometer, constructed in our laboratory, was used with a glass electrode. A vacuum tube, UX 54A,(9) made by Matsuda, Co. in Japan was used in this circuit. The characteristics of the tube are shown as follows:

filament potential	2.0 volt
plate potential	6.0 volt
screen grid potential	4.0 volt
control grid potential	4.0 volt
filament current	0.205 A.
plate current	40 μA.
screen grid current	297 μA.
control grid current	2×10^{-14} A.
mutual conductance	22 $\mu\Omega$

The working circuit is shown schematically in Fig. 1.

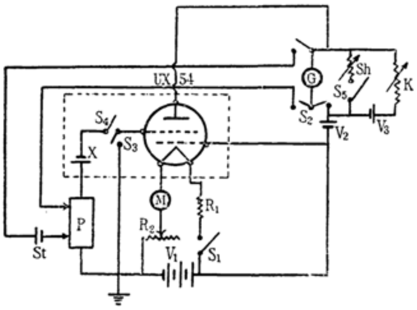

Fig. 1.—The working circuit of the vacuum tube potentiometer.

The component parts of the meter are given here for reference.

V_1: 6 volt battery
V_2: 3 volt battery
V_3: 1.5 volt battery
R_1: 10 ohm rheostat
R_2: 50 ohm rheostat
20,000 ohm rheostat
K: 3,000, 1,500 and 200 ohms variable resistances
S_1, S_2: switches
S_2, S_3, S_4: three pole three throw switches
Sh: galva shunt
G: galvanometer
M: milliammeter
X: glass electrode cell
P: Leeds and Northrup potentiometer
St: standard cell

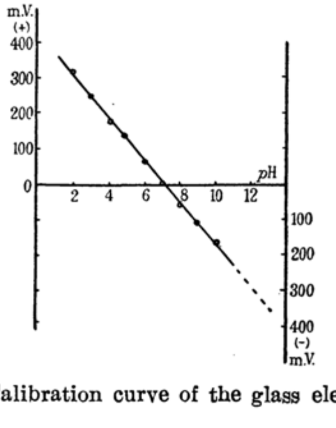

Fig. 2.—Calibration curve of the glass electrode.

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(9) Yoshimura, This bulletin, **12**, 359, 443 (1937).

The glass electrode was checked frequently against the Clerk-Lubs series buffer solutions. The calibration curve plotted e. m. f. vs. the pH is indicated in Fig. 2. The quantitative relation between e. m. f., E, observed, and the pH value is formulated as

$$E=0.43-0.0001983\,\mathrm{T}\,p\mathrm{H}$$

Results and Discussion

(A) Hydrolyses of tungstate, molybdate and chromate.

When a salt of a weak acid dissolves in aqueous solution, the hydrolysis of anions reaches a definite equilibrium for which the generalized reaction is

$$n\mathrm{A}^{a-}+m\mathrm{H_2O} \rightleftarrows p\mathrm{B}^{b-}+q\mathrm{OH}^- \qquad (1)$$

and when we take concentration of each constituent in place of activity, in dilute solution, putting

$$[\mathrm{A}^{a-}]=\mathrm{C}(1-x),\ [\mathrm{B}^{b-}]=\frac{p}{n}\mathrm{C}x,$$

$$\text{and } [\mathrm{OH}^-]=\frac{q}{n}\mathrm{C}x,$$

where x is the degree of hydrolysis and C the concentration, the hydrolysis constant, K_h, may be given, as a first approximation, by the expression:

$$\mathrm{K}_h=\frac{[\mathrm{B}^{b-}]^{p/n}[\mathrm{OH}^-]^{q/n}}{[\mathrm{A}^{a-}]}=\frac{1}{\mathrm{C}}\left(\frac{p}{q}\right)^{p/n}[\mathrm{OH}^-]\frac{p+q}{n}. \qquad (2)$$

Hence,

$$p\mathrm{OH}=-\frac{n'}{p+q}\left(\log \mathrm{K}_h-\frac{p}{n}\log\frac{p}{q}\right)-\frac{n}{p+q}\log \mathrm{C}$$

or

$$p\mathrm{H}=14+\frac{n}{p+q}\left(\log \mathrm{K}_h-\frac{p}{n}\log\frac{p}{q}\right)+\frac{n}{p+q}\log \mathrm{C} \qquad (3)$$

that is to say, a linear relationship should be held between pH and log C. Consequently, the differential quotient of the pH with respect to the logarithm of the concentration should be constant, i. e.,

$$\frac{dp\mathrm{H}}{d\log \mathrm{C}}=\frac{n}{p+q}. \qquad (4)$$

In a special case, $p=1$, we have

$$\frac{dp\mathrm{H}}{d\log \mathrm{C}}=\frac{n}{1+q} \qquad (4a)$$

or with respect to the degree of dilution, V, we obtain

$$\frac{dp\mathrm{H}}{d\log \mathrm{V}}=-\frac{n}{1+q} \qquad (4b)$$

as proposed by P. Souchay⁽¹⁰⁾.

According to equation (3) if we assume that the hydrolytic processes of normal molybdate and tungstate in dilute solution can be formulated as

$$2\mathrm{XO_4}^{--}+\mathrm{H_2O}\rightleftarrows\mathrm{X_2O_7}^{--}+2\mathrm{OH}^- \qquad (1a)$$

and the ionic hydration as well as the other poly-anions formation can be neglected in these cases, the values of solutions may be evaluated as

$$p\mathrm{H}=14+2/3(\log \mathrm{K}_h+1/2\log 2)+2/3\log \mathrm{C} \qquad (3a)$$

or

$$\frac{dp\mathrm{H}}{d\log \mathrm{C}}=\frac{2}{3}$$

that is to say, the slope of the curve plotted pH vs. $-\log$ C should be $-2/3$.

In the same way, in the hydrolytic process of chromate, which has been assumed to follow the reaction

$$\mathrm{CrO_4}^{--}+\mathrm{H_2O}\rightleftarrows\mathrm{HCrO_4}^-+\mathrm{OH}^- \qquad (5)$$

instead of

$$2\mathrm{CrO_4}^{--}+\mathrm{H_2O}\rightleftarrows\mathrm{Cr_2O_7}^{--}+2\mathrm{OH}^- \qquad (6),$$

the slope of the curve should be $-1/2$ instead of $-2/3$.

As shown in figure 3, in the cases of molybdate and tungstate, linear relationships exist between pH and $-\log$ C from C=0.1 to 0.001 mol. and the slope of each curve is nearly equal to $-2/3$. Agreement between the calculated and the observed values is excellent. On the other hand,

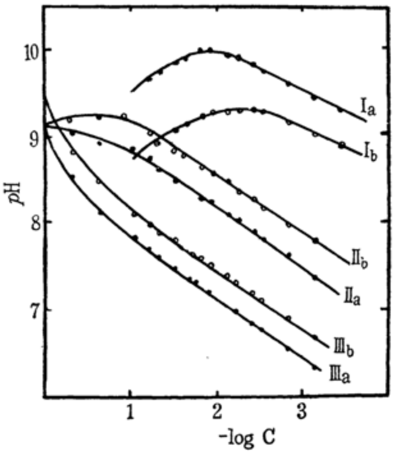

Fig. 3.—Hydrolyses of chromates, molybdates and tungstates.

Ia: Sodium chromate
Ib: Potassium chromate
IIa: Sodium molybdate
IIb: Potassium molybdate
IIIa: Sodium tungstate
IIIb: Potassium tungstate

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(10) P. Souchay, *Bull. Soc. Chim. France*, **1948**, 433.

Table 1

*p*H Values of Chromates, Molybdates and Tungstates Solutions at Varying Dilutions at 30°C.

Dilution (liters/mol.)	$-\log C$	Na_2CrO_4	K_2CrO_4	Na_2MoO_4	K_2MoO_4	Na_2WO_4	K_2WO_4
10	1.00	9.49	8.72	8.88	9.18	7.84	8.10
16	1.20	9.63	8.86	8.72	9.00	7.67	7.99
20	1.30	9.71	8.90	8.58	8.98	7.60	7.91
32	1.51	9.83	9.07	8.50	8.82	7.45	7.80
40	1.60	9.89	9.12	8.45	8.77	7.39	7.71
64	1.81	9.97	9.21	8.31	8.65	7.24	7.58
80	1.90	10.00	9.26	8.26	8.59	7.18	7.52
128	2.11	9.93	9.28	8.10	8.46	7.05	7.37
160	2.20	9.90	9.30	8.04	8.38	6.97	7.33
320	2.51	9.73	9.28	7.80	8.17	6.75	7.12
640	2.81	9.59	9.16	7.60	7.98	6.53	6.90
1280	3.11	9.44	9.04	7.38	7.78	6.34	6.67
2560	3.41	9.27	8.88	—	—	—	—

in the case of chromate, the slope of the curve at lower concentrations agrees closely with $-1/2$. Although another slope having the opposite sign is also found at higher concentrations, it may probably be attributable to the effect of the secondary dissociation of bichromate ion.

The *p*H values of sodium chromate, molybdate and tungstate as well as potassium chromate, molybdate and tungstate solutions measured at varying dilutions are tabulated in Table 1. From these experimental values, we obtain a generalized empirical formula governing the *p*H values of the salt solutions with concentrations over the concentration range 0.1—0.001 mol. as follows:

$$pH = a + b \log C$$

where the constants a and b may be evaluated by the method of least squares from the experimental data. Their numerical values are summarized in Table 2.

Table 2

a and b for Chromates, Molybdates and Tungstates

Salt	a	b
Sodium Chromate	11.00	0.520
Potassium Chromate	10.50	0.485
Sodium Molybdate	9.60	0.712
Potassium Molybdate	9.85	0.675
Sodium Tungstate	8.50	0.701
Potassium Tungstate	8.80	0.683

Since the experimental results obtained by the hydrolysis of these salts are in good agreement with the theoretical values from equation (1a), the present investigation gives a confirmation for the existence of dimolybdate and ditungstate ions, $Mo_2O_7^{--}$ and $W_2O_7^{--}$ as well as bichromate ion, $HCrO_4^-$, in dilute solution, and it also gives a

Table 3

Hydrolyses of Chromates, Molybdates and Tungstates at Varying Dilutions (30°C.)

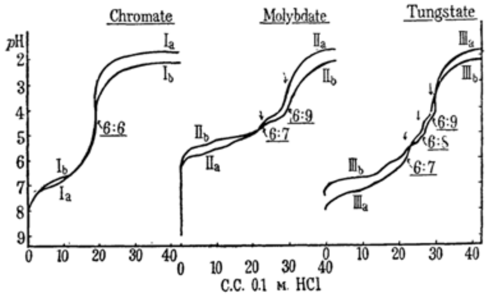
Dilution	Degree of Hydrolysis (X)						Hydrolysis Constant (K 1)					
Liters/mol.	Na_2CrO_4 $(\times 10^2)$	K_2CrO_4 $(\times 10^2)$	Na_2MoO_4 $(\times 10^4)$	K_2MoO_4 $(\times 10^4)$	Na_2WO_4 $(\times 10^5)$	K_2WO_4 $(\times 10^5)$	Na_2CrO_4 $(\times 10^6)$	K_2CrO_4 $(\times 10^7)$	Na_2MoO_4 $(\times 10^{14})$	K_2MoO_4 $(\times 10^{13})$	Na_2WO_4 $(\times 10^{17})$	K_2WO_4 $(\times 10^{18})$
10	—	—	0.76	1.51	0.69	1.26	—	—	2.12	1.72	1.66	0.98
16	—	—	0.84	1.60	0.75	1.56	—	—	1.85	1.28	1.31	1.20
20	—	—	0.76	1.91	0.80	1.63	—	—	1.70	1.74	1.26	1.08
32	—	—	1.01	2.11	0.90	2.02	—	—	1.62	1.47	1.15	1.29
40	—	—	1.13	2.36	0.98	2.06	—	—	1.79	1.64	1.18	1.09
64	—	—	1.31	2.86	1.11	2.43	—	—	1.76	1.83	1.07	1.12
80	0.80	—	1.46	3.11	1.21	2.65	0.80	—	1.93	1.88	1.11	1.16
128	1.09	—	1.61	3.69	1.44	3.00	0.93	—	1.63	1.96	1.17	1.05
160	1.27	0.32	1.75	3.84	1.49	3.42	1.01	0.64	1.69	1.77	1.03	1.25
320	1.72	0.61	2.02	4.73	1.80	4.22	0.93	1.16	1.29	1.79	0.91	1.17
640	2.49	0.93	2.55	6.11	2.17	5.08	0.97	1.34	1.29	1.78	0.80	1.03
1280	3.53	1.10	3.07	7.71	2.80	5.99	0.97	0.94	1.13	1.79	0.86	0.84
2560	4.77	1.94	—	—	—	—	0.89	1.47	—	—	—	—
Average.							0.93	1.11	1.67	1.72	1.13	1.11

confirmation for the similarity between the constitution of molybdate and tungstate as well as the dissimilarity between that of chromate and molybdate or chromate and tungstate.

Degrees of hydrolysis and the hydrolysis constants calculated from the pH values observed, by using equation (3a), are summarized in Table 3. Deviations at higher concentrations are not unexpected since activities have been ignored. On the one hand, from the facts that the degree of hydrolysis of molybdate is always greater than that of tungstate having the same concentration and the average value of the hydrolysis constant of the former is about a thousand times as great as the latter, as shown in Table 3, and also from the fact that pH values of the salt at the same dilution decrease in the order of chromate, molybdate and tungstate, as shown in figure 3, we may conclude that the strength of the acids increases with the atomic weights of these acidic metals, that is, in the order of chromic, molybdic and tungstic acids. On the other hand, by comparing the pH values of sodium tungstate with those of potassium tungstate, we find that potassium salt has greater pH values than those of the corresponding sodium salt, as in the cases of molybdates and tungstates. It may be attributable to the difference in the effect of the ionic size of the cations.

(2) Potentiometric titration of chromate, molybdate and tungstate with hydrochloric acid.

Data obtained by potentiometric titrations of normal salt solutions varying from 0.02 M to 0.1 M in molybdate ion or tungstate ion with 0.1 M hydrochloric acid at 30°C. are plotted as pH vs. the volume of 0.1 M hydrochloric acid added, as indicated in figure 4.



(a) (b) (c)

Fig. 4.—Potentiometric titration of sodium chromate, molybdate and tungstate with hydrochloric acid.

I a:	0.1 M Na_2CrO_4	I b:	0.02 M Na_2CrO_4
II a:	0.1 M Na_2MoO_4	II b:	0.02 M Na_2MoO_4
III a:	0.1 M Na_2WO_4	III b:	0.02 M Na_2WO_4

Data at different concentrations give exactly similar plots, and the displacements of the curves due to the dilution effects occur in each case. Curve Ia in figure 4a, curve IIa in figure 4b and curve IIIa in figure 4c indicate the titration curves of 0.1 M chromate, molybdate and tungstate with 0.1 M hydrochloric acid, while curve Ib, and curve IIb and curve IIIb in each figure indicate the titrations of 0.02 M of those salts with 0.1 M hydrochloric acid, respectively. Curves obtained for the higher concentration are steeper than those for the lower one. In figure 4b and 4c, two steep inflections occur in each curve at a XO_4^{--} to H^+ mol-ratios, 6:7 and 6:9, which have been attributed to the formation of the so-called paramolybdate and meta-molybdate ions, i. e., $HMo_6O_{21}^{5-}$ and $H_3Mo_6O_{21}^{3-}$, respectively, by Jander(4) and other authors(11)(12). The corresponding poly-anions of tungstate, para- and meta-tungstates, were observed prominently in the present investigation, though the pH ranges at which they are formed are different from those of molybdates. A steady inflection is revealed both in the titration curves of molybdate and tungstate, but it is not sufficiently pronounced. It is probably attributed to the existence of the poly-anion having the molar ratio, 6:4, that is, the formation of trimolybdate, $Mo_3O_{11}^{4-}$ as well as that of tritungstate, $W_3O_{11}^{4-}$, as suggested by Jander(4), but it could not be decided conclusively in this paper. Another steeper inflection at the mol-ratio, 6:8 occurs in titration curves of tungstate, IIIa and IIIb in figure 4c. It may be attributed to the existence of $H_2W_6O_{21}^{4-}$, but it is also not so pronounced as in the cases of para- and meta-tungstates. It has not been reported previously.

The equilibria between these poly-anions of tungstate, by analogy with those of molybdate may be formulated as follows:

(1) $6WO_4^{--}+4H^+=2W_3O_{11}^{4-}+2H_2O$
(2) $2W_3O_{11}^{4-}+3H^+=HW_6O_{21}^{5-}+H_2O$
or $6WO_4^{--}+7H^+=HW_6O_{21}^{5-}+3H_2O$
(3) $2HW_6O_{21}^{5-}+2H^+=2H_2W_6O_{21}^{4-}$
or $6WO_4^{--}+8H^+=H_2W_6O_{21}^{4-}+3H_2O$
(4) $HW_6O_{21}^{5-}+2H^+=H_3W_4O_{21}^{3-}$
or $6WO_4^{--}+9H^+=H_3W_6O_{21}^{3-}+3H_2O$

The mol-ratio and the pH ranges at which these poly-anions are formed are summarized in Table 4. Regarding to the titration curve of

Table 4
Mol-ratios and the pH Ranges of Poly-anions in Dilute Solutions

pH range	Mol-ratio Na_2MoO_4:HCl	Poly-anion
5.2	6 : 4	$Mo_3O_{11}^{4-}$
4.3—4.8	6 : 7	$HMo_6O_{21}^{5-}$
—	—	—
3.4—4.2	6 : 9	$H_3Mo_6O_{21}^{3-}$
pH range	Mol-ratio Na_2WO_4:HCl	Poly-anion
6.5	6 : 4	$W_3O_{11}^{4-}$
5.3—5.9	6 : 7	$HW_6O_{21}^{5-}$
4.5—4.9	6 : 8	$H_2W_6O_{21}^{4-}$
3.5—4.3	6 : 9	$H_3W_6O_{21}^{3-}$

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(11) P. Souchay, *Ann. Chim.* **18** 61, 73, 169 (1934).
(12) G. Biehler, *Ann. Chim.* (12) **2**, 189 (1947).

chromate, no inflection but that at the mol-ratio, 1:1 could be found. It is attributable to the formation of bichromate ion, $HCrO_4^-$, as has been known. The further investigation on the electrolytic behaviors and the constitution of these poly-anions will be reported in the subsequent papers of this series.

Summary

(1) A vacuum tube potentiometer constructed in our laboratory has been used for the pH measurements with a glass electrode.

(2) A mathematical expression for the hydrolytic process has been given as a linear relation between the pH values and concentrations of the solutions.

(3) Hydrolyses of chromates, molybdates and tungstates in dilute solutions have been observed.

(4) The existence of dimolybdate and ditungstate ions, $Mo_2O_7^{--}$ and $W_2O_7^{--}$, as well as that of bichromate ion, $HCrO_4^-$, in dilute solutions were confirmed by measuring the pH values at varying dilutions.

(5) An empirical formula for expressing the relationships between the pH values and concentrations of the solutions was proposed for chromate, molybdate and tungstate solutions.

(6) The similarities of the electrolytic behaviors between tungstate and molybdate as well as the dissimilarities of those between chromate and molybdate or between chromate and tungstate have been ascertained by means of potentiometric studies.

(7) It has been observed by these studies that the strength of the acids increases with the atomic weights of these acidic metals.

(8) The existence of para- and meta-poly-anions of tungstate as well as those of molybdate were confirmed by potentiometric titration of molybdate or tungstate with hydrochloric acid.

(9) A steady inflection at the mol-ratio, 6:4, is revealed both in molybdate and tungstate solutions, but it is not sufficiently pronounced. Another break at the mol-ratio, 6:8, was found in the titration curve of tungstate solution.

(10) No break but that at the mol-ratio, 1:1, which is attributable to the formation of bichromate ion could be found in the titration curve of chromate. It gives further confirmation of the dissimilarity between chromate and molybdate as well as tungstate.

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