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

II. Conductometric Studies on the Chromate, Molybdate and Tungstate Ions

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Since the initial development of the alternating-current conductivity bridge by Kohlrausch⁽¹⁾, various technical advances⁽²⁾ have been made in the source, in the bridge, or in the cell design and detection of the alternating-current signal. Though a properly constructed telephone receiver⁽³⁾ has been used, in general, as a suitable detector for determining the setting of the alternating-current bridge, the nervous strain of listening to very weak notes is still unavoidable, especially in the case of high resistance.

As a result of advances in the field of electronics, however, the electric eye⁽⁴⁾ and the cathode-ray oscillograph⁽⁵⁾ have been proposed for this purpose.

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(1) F. Kohlrausch, *Z. physik. Chem.*, **2**, 561 (1888).

(2) G. Jones and R. C. Josephs, *J. Am. Chem. Soc.*, **50** 1049 (1928); P. H. Dike, *Rev. Sci. Instruments*, **2**, 379 (1931); T. Shedlovsky, *J. Am. Chem. Soc.*, **52**, 1793 (1930).

(3) E. W. Washburn and K. Parker, *J. Am. Chem. Soc.*, **39**, 238 (1917).

(4) Hovorka and Mendenhall, *J. Chem. Education*, **16**, 239 (1939).

(5) Lamson, *Rev. Sci, Instruments*, **9**, 272 (1938).

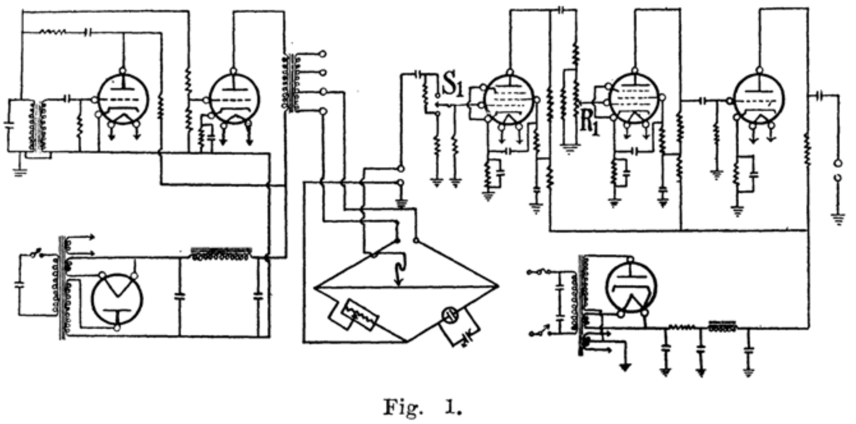

Fig. 1.

In the present investigation, measurements of the equivalent conductivities of chromate, molybdate and tungstate as well as conductometric titrations of these salts with hydrochloric acid have been carried out by using cathode-ray oscillograph as a detector for increasing the sensitiveness of the bridge setting and performing the rapid measurements.

Experimental

(1) **Materials.** — Conductivity water having a specific conductivity of 1.6 to 2.4×10^{-6} mho used in this experiment was purified by distillation according to the procedure described in the previous paper(6) of this series. The constant boiling fraction of hydrochloric acid was diluted to the desired concentration for use in the conductometric titrations.

All the salts used in the present investigation were purified by the repeated recrystallization from conductivity water as described in the previous paper(6). After desiccating the salts in vacuo at room temperature, the crystalline water and the composition of the salts were checked by gravimetric analysis.

The solutions used for conductometric measurements were prepared, directly, by dissolving the salt in carbonate-free conductivity water and diluted to a desired concentration before each run.

(2) **Apparatus.** — Schematic diagrams of the apparatus used for the conductometric measurement in the present investigation are given in Fig. 1. A Shimazu KR-2 type Kohlrausch bridge (B), made in Japan, has been used for this purpose with 1000 cycle alternating-current supplied by an audio-frequency oscillator (A). The bridge output voltage is amplified by a three-stage variable amplifier (C), and then supplied to the vertical deflecting plate of a cathode-ray oscillograph. Dotted lines surrounding each unit of the set indicate the electrostatic shielding. Although a simple cathode-ray oscillograph was used previously by W. Juda and his co-workers(7) as a detector of the bridge setting, a Du Mont 208 type cathode-ray oscillograph has been successfully used in this experiment. When the circuit is in action, any wave pattern on the cathode-ray screen indicates the unbalanced bridge, while a single straight line indicates the balanced bridge.

An unbalance of about 0.1 ohm could be detected and the sensibility of detection could be controlled as desired by adjusting R_1 and S_1 in Fig. 1, the gain control of the cathode-ray oscillograph.

While a conductance cell of the modified Jones and Bollinger type(8) consisting of a glass vessel in which two platinum plates of 1.5 cm in diameter are fixed in parallel and platinized in ordinary manner, was used for the measurements of specific conductivity, two platinized platinum wires of 4 cm. in length and 1 mm. in diameter fused in a glass bead were used as the cell electrodes for the conductometric titration in order to attain a rapid equilibrium.

The conductance cell was immersed in a water thermostat whose temperature has been kept at 25 ± 0.05°C. for the specific conductivity measurements, and at 35 ± 0.05°C. for conductometric titration, since the room temperature was as high as 32—33°C.

Results and Discussion

(1) Equivalent Conductivities of Sodium chromate, *Molybdate and Tungstate*.

—The equivalent conductivities of sodium chromate, molybdate and tungstate measured in this experiment at varying dilution are plotted against $\sqrt{10^3 C}$ or $\log V$, as shown in Fig. 2 and Fig. 3. Since the equivalent conductivities of these salts increase rapidly with the dilution, especially at extreme dilution, the limiting

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(6) K. Pan and T. M. Hseu: This bulletin, **26**, 126 (1953).

(7) G. Jones, K. Myels and W. Juda, *J. Am. Chem. Soc.*, **62**, 2919 (1940).

(8) G. Jones and G. M. Bollinger, *J. Am. Chem. Soc.*, **53**, 411 (1931).

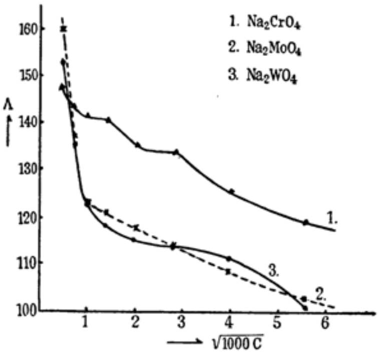

Fig. 2.—Λ and $\sqrt{1000 \times C}$.

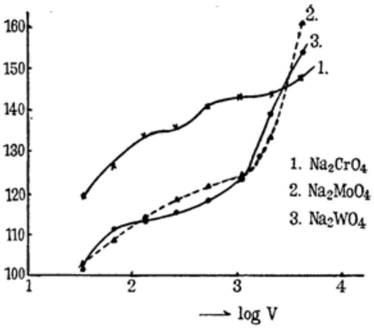

Fig. 3.—Λ and log V.

value of equivalent conductivity of each salt at infinite dilution can not be estimated in the usual way. It may be attributable to the increasing degree of hydrolysis of these salts in dilute solutions and therefore, is probably due to the fact that, as the result of hydrolysis, the steady increase in the OH^- ion would lead to a rapid increase in conductivity of each salt solution, owing to the great equivalent ionic conductivity of the OH^- ion. These results are in good agreement with those obtained in the previous paper⁽⁶⁾ which considered the hydrolytic process of molybdates and tungstates as follows:

$$2XO_4^{--} + H_2O = X_2O_7^{--} + 2OH^-$$

In this case, as degree of hydrolysis increase with the dilutions, x mol. of XO_4^{--} ion will be replaced by $x/2$ mol. of $X_2O_7^{--}$ and x mol. of OH^- ion which would lead to a rapid increase in conductivity.

Throughout the entire experimental concentration range, the equivalent conductivity of chromate is greater than those of molybdate or tungstate. It may be attributable to the different type of hydrolysis, as shown in the previous paper⁽⁶⁾, for the chromate ion,

$$CrO_4^{--} + H_2O = HCrO_4^- + OH^-$$

The similarity between the former, i. e. molybdate and tungstate as well as the dissimilarity between the latter, i. e. chromate and molybdate or tungstate, is confirmed also in this experiment.

Table 1

Equivalent Conductivities of Sodium Chromate, Molybdate and Tungstate at Varying Dilutions at 25°C.

Dilution, V (l./equiv.)	log$V$	$\sqrt{10^3 C}$	Equivalent Conductivities		
			Na_2CrO_4	Na_2MoC_4	Na_2WO_4
32	1.51	5.59	119.3	102.5	101.0
64	1.81	3.95	125.6	108.4	111.1
128	2.11	2.80	133.9	113.8	113.5
256	2.41	1.98	135.4	117.9	115.2
512	2.71	1.39	140.6	121.3	117.9
1024	3.01	0.99	142.1	123.5	123.0
2048	3.31	0.70	143.2	135.5	138.9
4096	3.61	0.49	147.8	160.5	153.2
	$\Lambda_{1024} - \Lambda_{32}$		23	21	22

The differences between Λ_{1024} and Λ_{32}, $\Lambda_{1024} - \Lambda_{32}$, for sodium chromate, molybdate and tungstate solutions are found to be 23, 21 and 22, respectively, approximately equal to 2×10. The Ostwald's rule concerning the basicity and the difference, $\Lambda_{1024} - \Lambda_{32}$, for solutions of sodium salts seems to be held also in this case, though it has been mentioned that the sodium salts of the majority of inorganic acids do not follow this rule, in general. If it is not due to the accidental coincidence, it may be taken as due to the fact that molybdic or tungstic acid, or even chromic acid is a kind of weak dibasic acid similar to the weak dibasic organic acids. It is in accordance with the fact that molybdic and tungstic acids have their mean dissociation constants of the order of 10^{-5} as reported by Bhagwat and Dhar⁽⁹⁾.

(2) **Conductometric Titration.**—Titration curves of 0.1 M and 0.02 M sodium chromate, sodium molybdate and sodium tungstate with 0.1 M HCl are shown in Fig. 4 and Fig. 5, respectively. Although one sharp break at the mol-ratio of 1:1, corresponding to the formation of bichromate ion is found in the titration curve of chromate, several kinds of breaks are found in the titration curves of molybdate and tungstate. Besides two sharp breaks at the points of XO_4^{--} to H^+ mol-ratios, 6:7 and 6:9, which have been taken

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(9) W. V. Bhagwat and N. R. Dhar, *J. Indian Chem. Soc.*, **6**, 807 (1929).

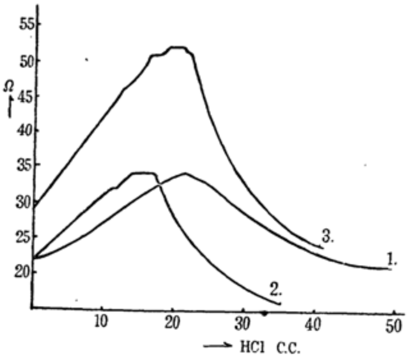

Fig. 4.—Conductometric titration of 0.1 M chromate, molybdate and tungstate with 0.1 M HCl.

1. 0.14 M Na_2CrO_4 15 cc.
2. 0.1 M Na_2MoO_4 15 cc.
3. 0.1 M Na_2WO_4 15 cc.

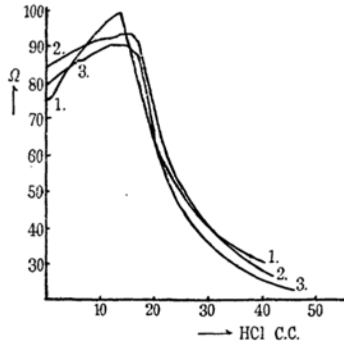

Fig. 5.—Conductometric titration of 0.02 M chromate, molybdate and tungstate with 0.1 M HCl.

1. 0.02 M Na_2CrO_4 75 cc.
2. 0.02 M Na_2MoO_4 75 cc.
3. 0.02 M Na_2WO_4 75 cc.

as the existence of para- and meta-poly-anions⁽¹⁰⁾ were observed both in molybdate and tungstate, a remarkable break at the mol-ratio, 6:8, was observed in the case of tungstate. It is in good accordance with the result obtained in the previous paper⁽⁶⁾. Another break at 6:5.5, or 12:11, was observed prominently in the titration curves of molybdate but fairly in those of tungstate. It seems to be possibly attributable to the mixture of $[W_3O_{11}]^{4-}$ and $[HW_6O_{21}]^{5-}$, or to the formation of another kind of poly-anion.

When the sodium tungstate is allowed to stand over night before using for titration, however, a steady inflection is found at the mol-ratio, 6:4, which may be attributed to the formation of trimolybdate or tungstate as described in the previous paper⁽⁶⁾, but we would not assert it until further confirmation could be obtained. The mol-ratios at which various kinds of recognizable breaks are revealed on the titration curves and the possible composition of the poly-anions are summerized in the Table 2.

Table 2

The Mol-ratios and Compositions of Poly-anions

Mol-ratio (calc.) $XO_4^{--}:H^+$	Poly-anion	Mol-ratio (obs.) $XO_4^{--}:H^+$ Na_2CrO_4	Na_2MoO_4	Na_2WO_4
6:4	$[X_3O_{11}]^{4-}$	—	6:4	6:4
6:5.5	$[HX_{12}O_{43}]^{13-}$?	—	6:5.5	6:5.5
6:6	$[HXO_4]^-$	1:1	—	—
6:7	$[HX_6O_{21}]^{5-}$	—	6:7	6:7
6:8	$[H_2X_6O_{21}]^{4-}$	—	—	6:8
6:9	$[H_3X_6O_{21}]^{3-}$	—	6:9.1	6:9

Summary

(1) Conductance measurements of sodium chromate, molybdate and tungstate solutions were carried out by using a Du Mont 208 type cathode-ray oscillograph as a detector of the Kohlrausch bridge setting.

(2) Equivalent conductivities of chromate, molybdate and tungstate at varying dilutions were measured at 25°C., but the limiting value of the equivalent conductivity of each salt at infinite dilution could not be estimated by the usual way, owing to the hydrolysis of these salts.

(3) The similarity between molybdate and tungstate as well as the dissimilarity between chromate and each of the two others were confirmed also in the present investigation.

(4) The difference $\Lambda_{1024}-\Lambda_{32}$ was found to be approximately equal to 2×10 for these sodium salts. It seems to indicate that either molybdic or tungstic or even chromic acid may be a kind of weak dibasic acid if Ostwald's rule is applicable.

(5) Besides two breaks at the XO_4^{--} to H^+ mol-ratios, 6:7 and 6:9 were found in the conductometric titration curves of molybdate and tungstate, a new sharp break at the mol-ratio 12:11 was observed prominently in the titration curves of molybdate but fairly in those of tungstate.

(6) A break at the mol-ratio, 6:8, which was reported in the previous paper, was found also in the titration curves of tungstate.

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