タングステンの電解分析に関する研究

第1報 電解中に起る酸性タングステン水溶液の行動

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A Study on Electrolysis of Tungstate

Part 1. Behavior of Acidified Aqueous Solution of Tungstate through Electrolysis

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I 緒言

Tungsten は他の金属に比べ，著るしく異なつた物理恒数を示すばかりでなく，化学的にもまた非常に特異な存在であり，特にその電析については興味深い行動を表わすものである。Tungsten の電析に関しては，遠く19世紀の中頃から始められ，それ以来多くの研究者達の撓まぬ努力を以てして，尚完成を見ていない。即ち C. G. Fink and F. L. Jones, (1)Holt and Kahlenberg, (2) Yntena, (3)鹿島—富岡, (4)鹿島—石原, (5)鹿島—福島, (6)河根, (7)等の諸氏の研究があげられる。そしてこれらの研究の大要を見ると，Na_2WO_4 水溶液または WO_3—NaOH の水溶液をアルカリ性緩衝液の存在で高温電解することに始まり，次いでその浴中に添加した Fe^{+++}, Co^{++}, Ni^{++}のような第二金属 Ion が Tungsten の電析に重要な役割を持つことを見出し，更にその理由は添加した第二金属 Ion と Tungsten とが形成する錯化合物によるものと考察している。しかも析出する Tungsten の量は僅少で到底実用には供し得べくもないことが報告されている。筆者は従来行われて来た Tungsten の電析法に検討を加え，他方 Tungsten と同族にある Cobalt 及び Molybden の電解浴を併せ考え，Tungsten の酸性浴に於ける電析の可能性を吟味する為，先ず酸性浴で Tungsten 水溶液がどんな行動を示すかを調査したので，ここに報告したい。

II 実験方法及び実験結果

1) 主な薬品及び器具

(i) Sodium Tungstate（石津）

(ii) U 字管（内径1 cm）

(iii) 白金 Coil（0.2mm の白金線 15cm を径 2.5mm の Coil にしたもの）

(iv) 白金板（0.5cm×0.5cm）

(v) Bright Dip で研磨した銅板

(vi) セレン整流器（島津）

(vii) 東洋 pH 試験紙（P.R., M.R., B.C.G., B.P.B., T.B., C.R.）

2) 酸性 Tungsten 水溶液の安定性の調査

殆んどすべての Tungsten に関する記録では，Na_2WO_4 水溶液が鉱酸酸性の下で，冷時 H_2

$WO_4 . H_2O$ の白色沈澱を，また熱時 H_2WO_4 の黄色沈澱を生ずると報じているが，沈澱法による Tungsten の分析に於て沈澱を酸で洗つた場合，濾紙上の Tungstic Acid がPseud Solution となつて濾液中に入るという事は見逃がせない事実であり，実際多量の Tungstic Acid が或濃度の酸性下に溶液として存在し得る。第１表はその大要を示したものである。

Table 1　Stability of Aqueous Solution of Sodium-tungstate in various pH

Concentration pH	$\frac{1}{100}$ Mol	$\frac{1}{10}$ Mol	1 Mol
7	Remains transparent, colorless for at least 3 Weeks.	Remains transparent, colorless for at least 3 weeks.	Remains transparent, colorless for at least 3weeks. After anight deposits colorless crystal.
6	(ditto)	(ditto)	(ditto) After 2 days deposits colorless crystal.
5	(ditto)	(ditto)	(ditto) After 4 days deposits colorless crystal.
4	(ditto)	(ditto)	(ditto) After a week deposits colorless crystal.
3	(ditto)	(ditto)	Remains transparent, slightly yellowish green solution for at least 3 weeks.
2	(ditto)	(ditto)	(ditto)
1	After about 6 hrs, white precipitate appears.	(ditto)	(ditto)

即ち1/100 Mol, 1/10 Mol, 1 Mol の3種の濃度の Na_2WO_4 水溶液50 cc 宛に，6 N. HCl を滴下し攪拌して生じた白色沈澱の消失するものを待つて更に滴下を繰返し pH 7 (P.R) pH 6 (M.R.) pH 5 (B, C.G.) pH 4 (B.P.B.) pH 3 (B.P.B.) pH 2 (T.B.) pH 1 (C.R.) を決定した後，夫々 10cc 宛を試験管に分ち取り，時間の経過に伴つて白濁または析出物の様子を観察したものである。

3) 前述に於て 1/10 Mol Na_2WO_4 水溶液では pH 1 から pH 7 にわたつて長時間，沈澱もなくまた結晶の析出も見られないことを知つたのでこの濃度の Tungsten 水溶液を standard とし，種々の条件の下で電解を試みた。条件，方法及び実験結果を Fig. 1—Table 2, Fig. 2—Table3, Fig. 3—Table 4に示す。

尚陽極遮蔽による装置に於て，陽極の代りに陰極を遮蔽すると，陰極室のみ青色となり陽極側の下面に多量の

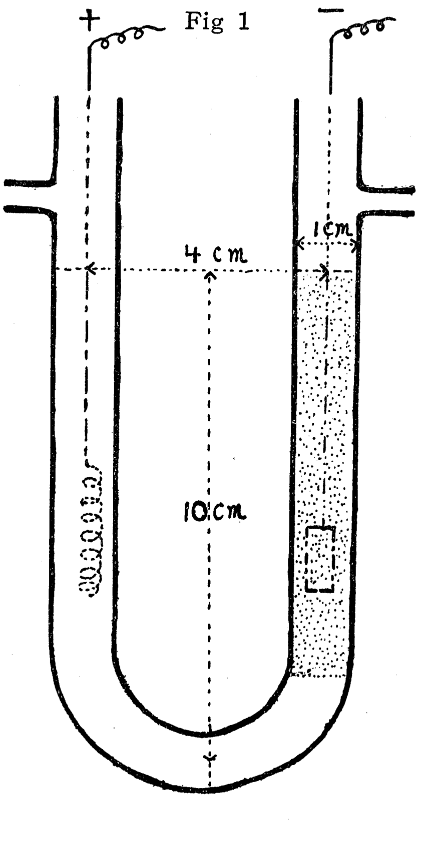


Fig 1

Table 2

Results of Electrolysing 1/10 Mol Sodium Tungstate Solution
acidified to various pH with HCl (Fig. 1)
Electrolysing condition: Dc=4A/dm^2, Pt-Cu electrodes
Room temperature, Aparatus shown in Fig. 1

pH	Behavior of Bath
7	About 5 mins. later, a blue substance appears on the cathode surface and gradually diffuses all over the cathode tube. About 20 mins. later, its color changes to that of 2% C_uSO_4, but soon afterwards it fades away rapidly to slight blue. In one hr. it becomes quite transparent.
6	As soon as the circuit is closed, a blue substance appears on the cathode surface and diffuses all over the cathode tube. The color gradually deepens in one hr. When the electrodes are taken out after one hour of electrolysis, the solution electrolysed returns to its original state in 5 hrs.
5	(The same condition applies here as mentioned in the case of pH6) The color deepens in 10 mins. In 12 hrs., however, the solution electrolysed for one hour returns to its original tsate.
4	(The same condition applies here as mentioned in the case of pH 6) The color deepens in 7 mins. In 26 hrs, the solution electrolysed for one hour returns to its original state.
3	(The same condition applies here as mentioned in the case of pH 6) The color deepens in 5 mins. In 27 hrs, the solution electrolysed for one hour returns to its original state.
2	(The same condition applies here as mentioned in the case of pH 6) The color deepens in 5 mins. In 40 hrs., the solution electrolysed for one hour returns to its original state.
1	(The same condition applies here as mentioned in the casse of pH 6) The color deepens in 5 mins. The colored substance fades away in 50 hrs. and produces white or yellow precipitate at the bottom of the U tube.

黄沈を生ずる。陽極遮蔽の効果は硫酸紙を用いる他に，青竹の表皮を削り取つた節のついたままの竹筒，または素焼でも同様である。また C—Cu, Pt—Hg, C—C, Pt—Pt など何れの組の電極でも電解の結果生ずる着色には差異が認められない。但し陽極に C を用いると時間の経過と共にその微粒が浴中に溶出してくる。対立極板の装置では pH が比較的大きい時にのみ Ozone が検知され，また何れの装置に於ても陰極電流密度 (D.C.) が大きい程，着色は容易であり，また陰極板上に赤黒い焼けが見られる。

4） 以上によつて安定な青色物質は陽極遮蔽による電解操作中に得られることを知つたので，更に pH 規正用の酸をとり変え，それによつて得た 1/10 Mol Na_2WO_4 の酸性浴を陽極遮蔽法で，しかも Pt—Pt 電極を使用して電解に附した。結果の大要は Table 5 の通りである。

III 考　察

河根，鉤両氏は(8) アルカリ浴に於けるタングステン水溶液の電解に於て，陽極側にパラタングステン酸ソーダが形成されると報告し，

Fig. 2

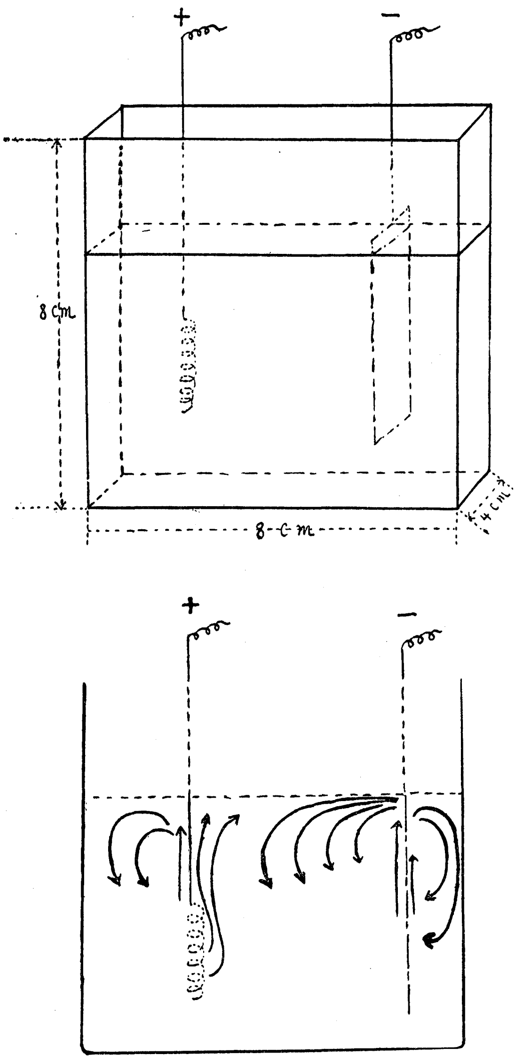
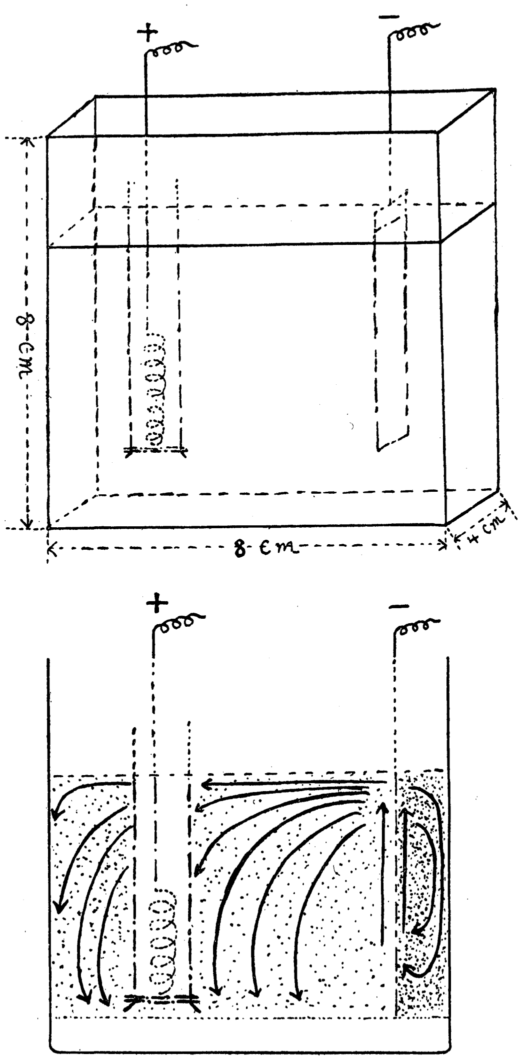


Fig. 3



$$5Na_2WO_4 - 7Na_2O = Na_{10}W_{12}O_{41}$$

として論じているが，このことは次の如く考えると容易に理解される。

$$Na_2WO_4 \rightleftarrows \underset{\substack{\downarrow\\ \ominus}}{2Na^+} + \underset{\substack{\downarrow\\ \oplus}}{WO_4^{--}}$$

$$2Na + 2H_2O = 2NaOH + H_2 \qquad WO_3 + O$$

電解によつて陽極側は WO_3 に富み，結局

$$5Na_2WO_4 + 7WO_3 = Na_{10}W_{12}O_{41} = 5Na_2O \cdot 12WO_3$$

に到達する。しかし，Na_2O と WO_3 との割合が種々考慮に入るから，反応条件によつて複雑な問題が潜むことは当然考えられる。また他方パラタングステン酸ソーダは Na_2WO_4 を中性または微酸性にする時生ずる事が知られている。この事も

$$Na_2WO_4 + 2H_2O \rightleftarrows 2NaOH + WO_3 + H_2O$$

Table 3
Results of Electrolysing 1/10 Mol Sodium Tungstate
Solution Acidified to Various pH with HCI
Electrolysing Conditions: Dc=4 A/dm^2, Pt-Cu electrodes
Room temperature, Apparatus: See Fig.2

pH	Behavior of Bath
7	A current, colorless and containing bubbles, such as is shown in Fig. 2 presents itself. There is an ozonic odor on the side of the anode.
6	ditto
5	As soon as electrolysis begins, a substance slightly blue appears on the surface of the cathode on the side opposite to the anode, but soon the color fades away, and in 10 mins. the solution becomes similar to that of pH 7.
4	As soon as electrolysis begins, the outer side space of the cathode is tinged with a gradually deepening blue color, until it becomes bright blue in 5 mins. 10 mins. later, the color begins to fades away and after 15 mins., only a current similar to that of pH 7 keeps going. There is a chloric odor on the side of the anode.
3	As soon as electrolysis begins, the outer side space of the cathode turns blue, and after three mins., the color is dark blue such as is observed in the case of pH4; 20 mins. later, the color begins to fades away and after about 30 mins., only a current similar to that of pH 7 keeps going; a strong chloric odor rises on the side of the anode.
2	As soon as electrolysis begins, the outer side space of the cathode turns blue, and after 3 mins., there also appears a slight blue on the surface of the cathode facing the anode; the color reaches the anode, spreading along the surface of the solution. But soon the color disappears and 30 mins. later, a current similar to that of pH 7 can be seen and a strong chloric odor rises on the side of the anode.
1	As soon as electrolysis begins, a blue color appears on both surfaces of the cathode, and after one min. the color looks like 2% C_uSO_4 along the surface of the solution between the electrodes; the outer side space of the cathode turns dark blue. But soon the color fades away, and 5 mins. later, a blue color sppears only on both surfaces of the cathode. 35 mins. later, only a current similar to that of pH 7 can be seen and a chloric odor is remarkable on the side of the anode.

に於て H^+ の添加により反応は右進し，従つて $Na_{10}W_{12}O_{41}$ が生成され得る。そこで Na_2WO_4 と $Na_{10}W_{12}O_{41}$ とを分子内の O 含有量に関して比較すれば

Na_2WO_4……………21.7%

$Na_{10}W_{12}O_{41}$ ………21.2%

であるから，パラ塩は一種の還元生成物と称し得る。舟木，浅田両氏(9)は $WO_3 \rightarrow W$ の還元過程に於て

$$WO_3 \rightarrow W_4O_{11} \rightarrow W_2O_5 \rightarrow W_4O_9 \rightarrow WO_2 \rightarrow W_2O_3 \rightarrow WO \rightarrow W$$

と考えるのが妥当であることを，平衡恒数の測定から報告しており，WO_3 から W への還元過程にある二三の物質の色調の変化は定説となつている。更に，Na_2WO_4 水溶液が種々の還元剤（$SnCl_2$,

Table 4

Results of Electrolysing 1/10 Mol Sodium Tungstate
Solution Acidified to Various pH with HCl
Electrolysing conditions: $Dc = 2\ A/dm^2$, Pt-Cu electrodes
Room temperature, Apparatus: See Fig. 3

pH	Behavior of Bath
7	10 mins. after electrolysis begins, a blue substance appears near the upper end of the cathode, and only the outer side space of the cathode is tinged with a deepening blue. After 30 mins. the color remains similar to that of 5% $CuSO_4$; after about 40 mins. the blue color begins to move along the surface towards the anode; one hr. later the space above the lower end level of the cathode is tinged with a color similar to that of 2%$CuSO_4$. When the electrodes are taken out after one hour's electrolysis, the color gradually fades away till the solution tums to the original state in one hour.
6	As soon as electrolysis begins, a blue substance appears on the both side surface of the cathode. The color of the outer side space of the cathode gradually deepens till it becomes dark blue in 25 mins. The blue on the side facing the anode begins to move towards the anode in not less than 4 mins., and 25 mins. later it remains bright blue. The space above the lower end level of the cathode is tinged slightly with blue in about one hour. when the electrodes are taken out after one hour's electrolysis, the color gradually fades away till the solution returns to the original state in 5 hrs.
5	As soon as electrolysis begins, a blue substance that has appeared on the both surfaces of the cathode diffuses in both directions and gradually deepens in color. At first, the outer side space of the cathode is deeper, but in one hour every part of the solution is unanimously of a deep blue color. The space below the lower end level of the cathode, however, remains almost colorless during the first 40 mins. when the electrodes are taken out after one hour's electrolysis, the color grndually fades away till the solution returns to the original state in about 10 hra.
4	As soon as electrolysis begins, a blue substance that has appeared on the both surfaces of the cathode diffuses in both directions and gradually deepens in color. At first the color in the onter side space of the cathode is deeper, but in one hour fhe whole of the solution is unanimously deep blue similar to that in the case of pH 5. The space below the lower end level of the cathode begins to color about 30 mins. later. When the electrodes are taken out after one hour's electrolysis, the color gradually fades away till the solution turns to the original state in about 15 hrs.
3	(ditto) The whole of the solution becomes dark blue after 30 mins. After one hour's electrolysis, the solution returns to the original state in about 20 hrs.
2	(ditto) The whole of the solution becomes dark blue after 20 mins. After one hour's electroysis, the solution returns to the original state in about 30 hrs.
1	(ditto) The whole of the solution becomes dark blue after 15 mins. After one hour's electrolysis, the solution returns to the original state in about 36 hrs.

Note:

1. A piece of perchment paper attached to the test tube is used to screen the anode.
2. A deposit white or yellow color is produced in great quantities in the anode chamber, and a chloric odor is remarkable.
3. The blue substance diffuses with the current shown in Fig. 3.
4. The coloring of the space below the lower end level of the cathode begins on the side of the anode firsf.

Table 5

Changes that Occur during Electrolysing 1/10 Mol Na_2WO_4 Solution Adjusted to pH 3 with Various Acids

Acids used	Electrolysing conditions	10 mius. after electrolysis	One hour after electrolysis	When concentrated after an hour's electrolysis	products
HCl	room temperature, 14V - 2A/dm$_2$	blue throughout	blue throughout	dark blue→blue→light blue→colorless	colorless needle-shaped crystal
H_2SO_4	ditto	ditto	ditto	ditto	colorless plate-shaped crystal
HNO_3	ditto	ditto	ditto	ditto	colorless needle-shaped crystal
H_3PO_4	ditto	light blue throughout	dark blue throughout	dark blue→blue→reddish purple	jelly-like green substance
CH_3COOH	no change	no change			
	90°C 14V - 5A/dm$_2$	light blue throughout	slightly dark blue	blue→light-purpl→colorless→light-yellow	jelly-like yellowish substance
$(COOH)_2$	rooom temperature, 14V - 2A/dm$_2$	no change	no change		
	90°C 14V - 5A/dm$_2$	faint blue throughout	light blue throughout	light blue→colorless→light yellow	jelly-like white substance

Note:

1. The greater the density of current is, the sooner the blue substance appears.
2. The greater the concentration of Na_2WO_4 is, the sooner the blue snbstance appears and the deeper its color is.

$Zn-HCl$, $TiCl_3$）によつて青色となることは，既に定性または定量分析に応用されており，タングステン酸塩の熔融還元生成物が Wolfram Bronze として用いられていることも衆知の通りである。

以上の諸報告を本にして，筆者の試みた実験結果を考察すれば，大体次の如くである。

1） 陰極に生成される青色の物質は使用した極板の種類には無関係であるが，pH の規正に用い