15. *Polarographic Study of Manganese, Technetium, and Rhenium.*

By R. Colton, J. Dalziel, W. P. Griffith, and G. Wilkinson.

The polarographic reduction of potassium permanganate, potassium pertechnetate, potassium per-rhenate, and potassium octacyanorhenate(V) has been studied in aqueous solution with a variety of supporting electrolytes. The polarographic reduction of manganese and rhenium carbonyls and carbonyl halides has been studied in non-aqueous solution, a quaternary ammonium salt being used as supporting electrolyte.

Three new valency states have been observed for technetium. A novel method of purification of the element is described and several analytical procedures are suggested.

The object of this work was to investigate and compare the valency states exhibited by the three elements manganese, technetium, and rhenium under different conditions. It was hoped that by comparing potassium pertechnetate and potassium per-rhenate especially this information would suggest differences in the stabilities of the oxidation states of the elements which could be exploited on the preparative scale.

The polarographic reduction of potassium permanganate with barium chloride as supporting electrolyte has been investigated.[1] It was found that the manganese was easily reduced to the 2+ state and at a higher potential to that of the metal itself.

No detailed polarographic study of technetium has been reported, although it has been

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[1] Stackelberg, Klinger, Koch, and Krath, *Tech. Mitt. Krupp Forschungsber.*, 1939, **2**, 59; *Arch. Eisenhuttenw.*, 1939, **13**, 249.

mentioned that technetium is reduced polarographically to the 4+ state in 2N-sodium hydroxide.[2]

The polarographic reduction of per-rhenate ion has been studied by Lingane,[3] Rulfs and Elving,[4] and Geyer.[5]

No previous polarographic work has been reported on the carbonyls and carbonyl halides of manganese and rhenium.

EXPERIMENTAL

Purification of Technetium.—The starting material was impure ammonium pertechnetate solution provided by the Atomic Energy Authority, Harwell. The solution contained other ammonium salts, but was known from spectrographic analysis to be free from rhenium and manganese.

The solution was evaporated almost to dryness twice with concentrated ammonia, and traces of a brown gelatinous precipitate were centrifuged off. The solution was evaporated to dryness and the ammonium pertechnetate reduced to technetium metal in a platinum boat by hydrogen at 350° as described by Cobble *et al.*[6] Unlike rhenium metal, technetium is reported to be insoluble in hydrogen peroxide,[7] but we have found it to be very soluble in bromine water (0·5 ml. of bromine per 10 ml. of water), especially on warming, as is rhenium.[8] The solution was evaporated to a small volume to expel the excess of bromine and then neutralised with potassium hydroxide. On evaporation a mixture of potassium bromide and potassium pertechnetate was obtained.

The bulk of the potassium pertechnetate was purified by recrystallisation from water (solubility of $KTcO_4$ *ca.* 12 g./100 ml.; of KBr *ca.* 70 g./100 ml.) and washing with alcohol.

Potassium pertechnetate could be recovered from the supernatant liquids, washings, and other residual solutions by addition of "nitron" acetate solution (5 g./100 ml.). The white precipitate of nitron pertechnetate was collected in a Schwartz–Bergkampf filter beaker and then kept in contact with 4N-ammonia solution for 2—3 days. This treatment converts the precipitate into nitron (insoluble), and a solution of ammonium pertechnetate is formed from which, after filtration and evaporation, the salt was obtained as fine white crystals. The purity was checked by quantitative conversion to the potassium salt by evaporation with a stoicheiometric amount of potassium hydroxide solution.

Potassium pertechnetate prepared by both methods gave identical polarographic results, confirming the high purity of both samples.

The procedure of reduction to the metal followed by subsequent dissolution in bromine water and nitron precipitation is recommended as an excellent method for recovery of technetium from laboratory residues.

Preparation of Other Compounds for Polarographic Study.—Potassium per-rhenate was prepared by dissolving pure rhenium metal (Johnson, Matthey and Co. Ltd.) in 20-vol. hydrogen peroxide, neutralising this with potassium hydroxide, and filtering off the precipitate of potassium per-rhenate. The compound was recrystallised twice from distilled water.

Potassium octacyanorhenate(V) was prepared from potassium hexaiodorhenate(IV) by the action of potassium cyanide in methanol.[9] Manganese [10] and rhenium carbonyls [11] and the corresponding pentacarbonyl halides [12] were prepared by the usual methods and purified by steam distillation, chromatography, and recrystallisation.

Polarographic Measurements.—All polarograms were recorded on a Tinsley Model 19/2 recording polarograph and against a saturated calomel electrode. All supporting electrolytes were of analytical grade and the solutions were de-aerated by oxygen-free nitrogen.

The valency states to which the elements were reduced were calculated by use of the Ilkovič [13]

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[2] Rogers, *J. Amer. Chem. Soc.*, 1949, **71**, 1507.
[3] Lingane, *J. Amer. Chem. Soc.*, 1942, **64**, 1001.
[4] Rulfs and Elving, *J. Amer. Chem. Soc.*, 1951, **73**, 3281.
[5] Geyer, *Z. anorg. Chem.*, 1950, **263**, 47.
[6] Cobble, Nelson, Parker, Smith, and Boyd, *J. Amer. Chem. Soc.*, 1952, **74**, 1852.
[7] Fried, *J. Amer. Chem. Soc.*, 1948, **70**, 442.
[8] Theobald and Stern, *Analyst*, 1952, **77**, 99.
[9] Colton, Peacock, and Wilkinson, *Nature*, 1958, **182**, 393.
[10] Closson, Buzbee, and Ecke, *J. Amer. Chem. Soc.*, 1958, **80**, 6167.
[11] Hieber, Schuh, and Fuchs, *Z. anorg. Chem.*, 1941, **248**, 243.
[12] For references see Abel and Wilkinson, *J.*, 1959, 1507.
[13] Kolthoff and Lingane, "Polarography," Vol. I, Interscience Publishers Inc., New York, 1952.

equation, $i_d/c = 607nD^{\frac{1}{2}}m^{\frac{2}{3}}t^{\frac{1}{6}}$, where i_d is the diffusion current (μamp.), c is the concentration (mmoles/l.), D is the diffusion coefficient (cm.^{2} sec.$^{-1}$), m is the rate of flow of mercury (mg./sec.), and t is the drop time. The value of D for the per-rhenate ion was taken[3] as $1{\cdot}37 \times 10^{-5}$ cm.^{2} sec.$^{-1}$, and this value was also assumed for the pertechnetate ion. The constant $m^{\frac{2}{3}}t^{\frac{1}{6}}$ was determined in the usual manner to be 2·20.

The reversibility of the waves was investigated[13] by plotting E against log $[i/(i_d - i)]$ and comparing the slope with the theoretical value of $0{\cdot}059/n$. The waves were shown to be diffusion-controlled by plotting h^2 against i_d.

The "n" values for the carbonyl reductions were checked by using cobalt octacarbonyl as reference.

RESULTS

Potassium permanganate in 2M-potassium chloride is reduced to Mn^{II} at about $-0{\cdot}1$ v, and this is further reduced to the metal at about $-1{\cdot}7$ v. Similar behaviour was observed in 0·1M-potassium cyanide solution. Potassium permanganate was not studied further as it was found that technetium behaved far more like rhenium, as was expected.

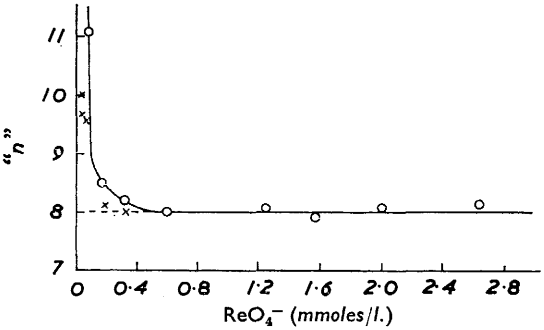


FIG. 1. *Polarographic reduction of per-rhenate ion; variation of "n" value with concentration.*

○ Present work. × Lingane.

Potassium Pertechnetate and Potassium Per-rhenate.—The polarographic reductions of these two compounds were compared, in a variety of supporting electrolytes, as follows.

(a) 2M-*Potassium chloride.* Lingane[3] found that potassium per-rhenate was polarographically reduced in 2M-potassium chloride to the rhenide state Re^{-I}, but the "n" values calculated from the Ilkovič equation varied with concentration, tending towards the theoretical value of 8 at the highest concentration studied. The reduction has now been examined over a wider concentration range and it has been found that when the concentration of per-rhenate ion exceeds 0·4mM, the "n" value is truly 8, but below this concentration it rises rapidly. This effect is shown in Fig. 1.

The wave is well defined although it always showed a slight maximum. It was also confirmed that the half-wave potential varied with concentration (Table 1). The polarographic behaviour of pertechnetate ion in 2M-potassium chloride is very similar to that of per-rhenate, but more dilute solutions must be used to obtain satisfactory results (Table 2). Above 0·1 mM the wave

TABLE 1. *Polarographic reduction of per-rhenate ion in 2M-potassium chloride.*

Concn. (mM)	2·67	2·05	1·57	1·25	0·62	0·32	0·16	0·08
i_d (μA)	105	80·8	58·5	48·6	24·0	12·7	6·5	4·3
$i_d/cm^{\frac{2}{3}}t^{\frac{1}{6}}$	17·7	17·8	17·2	17·7	17·6	18·0	18·6	24·4
n	8·04	8·09	7·90	8·04	8·00	8·20	8·40	11·20
$E_{\frac{1}{2}}$ (v)	−1·61	−1·57	−1·56	−1·56	−1·55	−1·55	−1·55	−1·55

TABLE 2. *Polarographic reduction of pertechnetate ion in 2M-potassium chloride.*

Concn. (mM)	0·094	0·075	0·063	0·037	0·030	0·024	0·012
i_d (μA)	3·8	3·2	2·6	1·55	1·24	0·96	0·60
$i_d/cm^{\frac{2}{3}}t^{\frac{1}{6}}$	18·3	19·4	18·7	19·0	18·8	20	23
n	8·3	8·8	8·5	8·6	8·5	9·09	10·5
$E_{\frac{1}{2}}$ (v)	−1·15	−1·145	−1·140	−1·14	−1·13	−1·12	−1·12

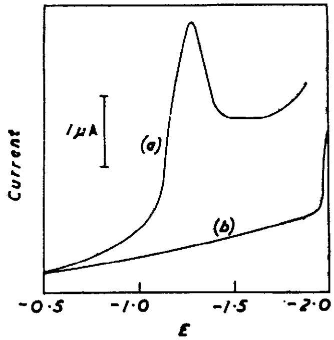
is distorted by a large maximum and this remains to a certain extent at all the concentrations studied (Fig. 2). In very dilute solutions the " *n* " values increase as for rhenium (Fig. 3).

In order to calculate the " *n* " values from the Ilkovič equation the value of the diffusion coefficient for the pertechnetate ion is assumed to be the same as for the per-rhenate ion. This assumption is justified since it is known that the pertechnetate and per-rhenate ions are of almost the same size [14] and any small error in D is reduced as only the square-root is used in the Ilkovič equation.

The assumed value of $D = 1{\cdot}37 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ gives a steady " *n* " value of 8·54. The deviation from 8·0 is probably due to the difficulties of measuring the limiting current accurately because of the maximum. The wave is highly irreversible, the plot of log $[i/(i_d - i)]$ against E being non-linear.

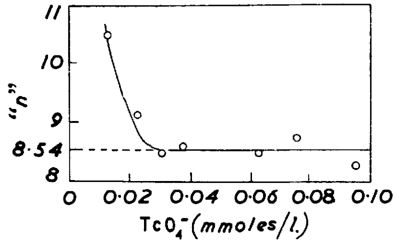
(b) 4M-*Perchloric acid.* Potassium pertechnetate showed no reduction in 4M-perchloric acid; the current merely increased gradually to the voltage of the reduction of the supporting electrolyte. This behaviour is in direct contrast to that of per-rhenate, which shows a well defined wave at about −0·4 v corresponding to a three-electron reduction.[3,4]

FIG. 2. *Polarogram of pertechnetate ion in* 2M-*potassium chloride* [(*a*) 0·037mM-$KTcO_4$; (*b*) *residual current of* 2M-KCl].



E, the decomposition voltage, is given in volts against S.C.E. in this and later diagrams.

FIG. 3. *Variation of " n " value with concentration for pertechnetate ion.*



(c) 4M-*Hydrochloric acid.* Per-rhenate ion is reported to be polarographically reduced to Re^{IV} in 4M-hydrochloric acid in a single wave.[3,4]

Pertechnetate ion is also reduced to the +4 state in 4M-hydrochloric acid, but a double wave is obtained, the components corresponding to a one- and a two-electron reduction, respectively. The waves are rather poorly defined (Fig. 4) with half-wave potentials (*vs.* S.C.E.) of −0·52 v and −0·68 v respectively.

Both waves are irreversible; the slopes of the log plot were 0·035 and 0·050, compared with required values of 0·059 and 0·029, respectively.

(d) 0·1M-*Potassium hydroxide.* Potassium per-rhenate in 0·1M-potassium hydroxide gave a large, poorly defined wave (Fig. 5). The " *n* " values from the Ilkovič equation were not constant, varying with concentration as shown in Table 3. However, it seems that per-rhenate ion is reduced to the rhenide (Re^{-1}) in 0·1M-potassium hydroxide.

TABLE 3. *Polarographic reduction of per-rhenate ion in* 0·1M-*potassium hydroxide.*

Concn. (mM)	1·01	1·01	0·71	0·49	0·49
i_d (μA)	48·0	48·0	34·5	18·0	18·0
$i_d/cm^{\frac{2}{3}}t^{\frac{1}{6}}$	21·6	21·6	18·3	16·7	16·7
n	9·8	9·8	8·3	7·6	7·6
$E_{\frac{1}{2}}$ (v)	−1·72	−1·72	−1·68	−1·66	−1·66

Pertechnetate, in marked contrast, is reduced only to the 4+ state in two stages, corresponding to a two- and a one-electron reduction at −0·85 and −1·15 v, respectively. The waves, especially the first one, are well defined (Fig. 6) and there is no marked variation of " *n* "

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[14] Ahrens, *Geochim. Cosmochim. Acta*, 1952, **2**, 155.

value with concentration (Table 4). Both technetium waves are irreversible, the slopes of both log plots being 0·077; theoretical values were 0·029 and 0·059.

(e) 0·1M-*Potassium cyanide.* Potassium cyanide is a very poor supporting electrolyte for the polarography of per-rhenate ion. A large wave was obtained which seemed to consist of two components, but they were so poorly defined that no reliable measurements could be made upon them, although they were possibly a two-electron and a four-electron reduction.

TABLE 4. *Polarographic reduction of pertechnetate ion in* 0·1M-*potassium hydroxide.*

	Concn. (mM)	i_d (μA)	$i_d/cm^{\frac{2}{3}}t^{\frac{1}{6}}$	n	$E_{\frac{1}{2}}$ (v)		Concn. (mM)	i_d (μA)	$i_d/cm^{\frac{2}{3}}t^{\frac{1}{6}}$	n	$E_{\frac{1}{2}}$ (v)
	0·130	1·24	4·95	2·25	−0·85		0·130	0·56	2·2	1·00	−1·14
	,,	1·20	4·80	2·20	,,		,,	0·56	2·2	1·00	,,
Wave A	0·108	1·04	4·60	2·05	−0·86	Wave B	0·108	0·56	2·6	1·20	−1·16
	,,	0·96	4·50	2·03	,,		,,	0·56	2·6	1·20	,,
	0·087	0·72	4·30	1·95	−0·85		0·087	0·36	2·15	0·95	−1·16
	,,	0·76	4·50	2·05	,,		,,	0·36	2·15	0·95	,,

Potassium pertechnetate gave a single well defined wave (Fig. 7) with a half-wave potential of −0·81 v, corresponding to a three-electron reduction to Tc^{IV}. The wave was irreversible, the slope of the log plot being 0·042 compared with the theoretical value for $n = 3$ of 0·019.

FIG. 4. *Polarogram of pertechnetate ion in* 4M-*hydrochloric acid* [(*a*) 0·130mM-$KTcO_4$; (*b*) *residual current of* 4M-HCl].

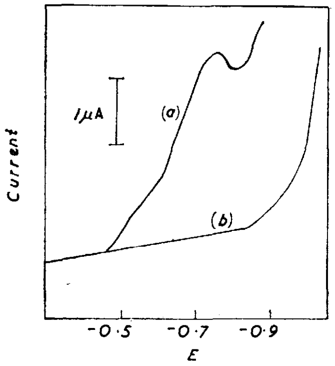

FIG. 5. *Polarogram of potassium per-rhenate in* 0·1M-*potassium hydroxide* [(*a*) 0·71mM-$KReO_4$; (*b*) 0·49mM-$KReO_4$; (*c*) *residual current of* 0·1M-KOH].

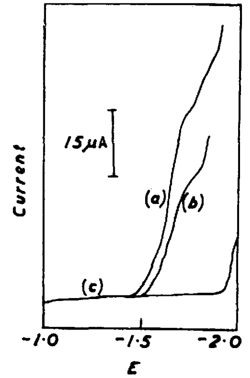

Table 5 summarises the results obtained for pertechnetate and per-rhenate ions.

TABLE 5. *Summary of oxidation states of technetium and rhenium from polarography.*

Supporting electrolyte	Per-rhenate				Pertechnetate			
2M-KCl		+7	−1			+7	−1	
4M-$HClO_4$		+7	+4 [3, 4]			no reduction		
4M-HCl		+7	+4 [3, 4]		+7	+6;	+6	+4
0·1M-KOH		+7	−1		+7	+5;	+5	+4
0·1M-KCN	+7	+5?;	+5	+1?		+7	+4	

It may be noted finally, with regard to the reduction of rhenium to the −1 state, that preliminary nuclear magnetic resonance measurements [15] have shown that the so-called rhenide ion is a complex ion with a rhenium–hydrogen bond of the type $[HRe(OH)(H_2O)_3]^-$, $[H_3Re(OH)_3H_2O]^-$, etc. Further work will be described subsequently.

Potassium Octacyanorhenate(v).—Potassium octacyanorhenate(v), $K_3Re(CN)_8$, was polarographed in 2M-potassium chloride and in 0·1M-potassium cyanide.

In potassium chloride the compound showed a well defined wave (Fig. 10), the half-wave potential being about −1·5 v (Table 6).

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[15] Colton, Dalziel, Griffith, and Wilkinson, *Nature*, 1959, **183**, 1755.

FIG. 6. *Polarogram of pertechnetate ion in* 0·1M-*potassium hydroxide* [(*a*) 0·130mM-$KTcO_4$; (*b*) 0·108mM-$KTcO_4$; (*c*) *residual current of* 0·1M-KOH].

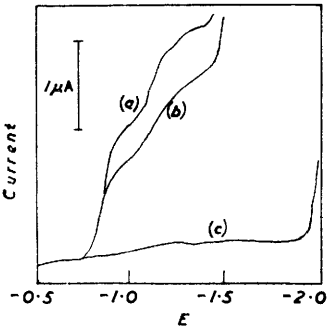


FIG. 7. *Polarogram of pertechnetate ion in* 0·1M-*potassium cyanide* [(*a*) 0·130mM-$KTcO_4$; (*b*) 0·108mM-$KTcO_4$; (*c*) *residual current of* 0·1M-KCN].

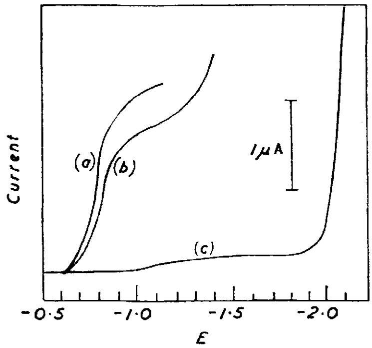


FIG. 8. *Polarogram of octacyanorhenate*(V) *in* 2M-*potassium chloride* [(*a*) 0·9mM-$K_3Re(CN)_8$; (*b*) 0·54mM-$K_3Re(CN)_8$; (*c*) *residual current of* 2M-KCl].

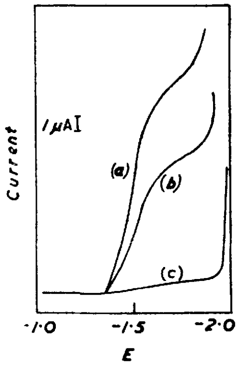


FIG. 9. *Polarogram of octacyanorhenate*(V) *in* 0·1M *potassium cyanide* [(*a*) 0·27mM-$K_3Re(CN)_8$; (*b*) *residual current of* 0·1M-KCN].

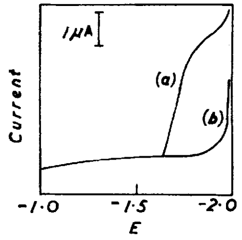


FIG. 10. *Polarogram of* $Re_2(CO)_{10}$ *in* 0·3M-*tetramethylammonium chloride in ethanol* [(*a*) 0·62mM-$Re_2(CO)_{10}$; (*b*) *residual current*].

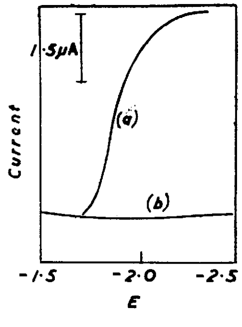
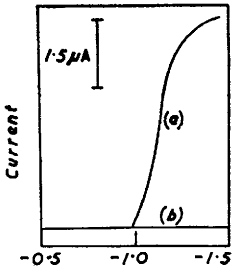


FIG. 11. *Polarogram of* $Mn_2(CO)_{10}$ *in* 0·3M-*tetramethylammonium chloride in ethanol* [(*a*) 0·65mM-$Mn_2(CO)_{10}$; (*b*) *residual current*].



In 0·1M-potassium cyanide another good wave was obtained (Fig. 11), the half-wave potential being about −1·75 v (Table 7).

TABLE 6. *Polarography of potassium octacyanorhenate*(V) *in* 2M-*potassium chloride.*

Concn. (mM)	1·8	0·9		0·54	0·378	0·378	0·378	
i_d (μA)	31·5	15·3	15·5	9·6	6·4	6·2	6·4	
$i_d/\text{cm}^{2/3}t^{1/6}$	7·95	7·73	7·82	7·77	7·77	7·73	7·77	Mean 7·79
$E_{\frac{1}{2}}$ (v)	−1·45	−1·50		−1·52	−1·52	−1·52	−1·52	

TABLE 7. *Polarography of potassium octacyanorhenate*(V) *in* 0·1M-*potassium cyanide.*

Concn. (mM)	1·8		0·9	0·54	0·27	
i_d (μA)	20·25	21·0	10·2	6·05	3·1	
$i_d/cm^{2/3}t^{1/6}$	5·09	5·27	5·14	5·09	5·23	Mean 5·16
$E_{\frac{1}{2}}$ (v)	−1·80		−1·76	−1·74	−1·72	

In order to calculate the " *n* " values it is necessary to make some assumption as to the value of the diffusion coefficient. Jezowska[16] found that the diffusion coefficient of the $[ReO_2(CN)_4]^{3-}$ ion is 0·7 × 10^{-5} cm.^{2} sec.$^{-1}$ and that in potassium chloride this ion is reduced to Re^{-1} and in potassium cyanide to Re^{+1}.

The ratio of " *n* " values for $K_3Re(CN)_8$ in the two supporting electrolytes studied is the same as the ratio of the $i_d/cm^{2/3}t^{1/6}$ values, *i.e.*, 7·79/5·16 = 1·504/1 = 6 : 4. In view of Jezowska's results it seems far more likely that the ratio is 6 : 4, that is, in potassium chloride $K_3Re(CN)_8$ is reduced to Re^{-1} and in potassium cyanide to Re^{+1}. If a rough calculation is made for D on this basis, the value obtained is 0·55 × 10^{-5} cm.^{2} sec.$^{-1}$ in fair agreement with Jezowska's value for the oxycyanide.

This interpretation is also in agreement with the behaviour of per-rhenate in potassium chloride and potassium cyanide.

Manganese and Rhenium Carbonyl Complexes.—The polarographic reduction of manganese and rhenium carbonyl and carbonyl halides was studied in absolute ethanol containing 0·3M-tetramethylammonium chloride as supporting electrolyte. The results are shown in Table 8.

TABLE 8. *Polarographic reduction of manganese and rhenium carbonyls and carbonyl halides.*

	$Mn_2(CO)_{10}$; S = 0·114						$Re_2(CO)_{10}$; S = 0·15			
Concn. (mM)	1·84	0·65	0·42	0·20	0·10	0·05	1·25	0·78	0·62	0·52
i_d (μA)	14·0	4·5	2·9	1·4	0·72	0·38	9·2	5·8	4·4	4·00
$i_d/cm^{2/3}t^{1/6}$	2·9	2·66	2·66	2·69	2·77	2·77	2·83	2·86	2·74	2·96
$E_{\frac{1}{2}}$ (v)	−1·16	−1·15	−1·15	−1·14	−1·14	−1·14	−1·83	−1·82	−1·82	−1·82

	$Mn(CO)_5I$; S = 0·17 †							$Re(CO)_5I$	$Re(CO)_5Cl$
Concn (mM)	2·62	1·73	1·64	0·31	0·15	0·08	0·04	3·93	0·77
i_d (μA)	19·8	13·2	10·6	2·3	1·12	0·60	0·30	15·2	2·7
$i_d/cm^{2/3}t^{1/6}$	2·91	2·94	(2·5)	2·86	2·88	2·88	2·88	2·96	—
$E_{\frac{1}{2}}$ (v)	−0·83	−0·79	−0·79	−0·79	−0·79	−0·78	−0·78	−1·18	−1·27

S = Slope of log plot. † Half-wave potentials for the bromide and chloride are −0·85 v and −0·91 v respectively.

All the waves were irreversible. It was found, in accordance with chemical evidence, that the halides were more easily reduced than the simple carbonyls and furthermore that in the halide series the half-wave potentials were in the sequence I < Br < Cl. In all cases the number of electrons gained in the reduction of each species was 2, so that reduction to Mn^{-1} and Re^{-1} occurred, presumably to the carbonyl hydride anions $[Mn(CO_5)]^{-1}$ [17] and $[Re(CO)_5]^-$.[18]

The value $n = 2$ was checked by comparison with reduction polarography of cobalt octacarbonyl[19] and oxidation polarography of ferrocene.[20]

The tetracarbonyl halides of manganese[12] and rhenium[21] were not reduced polarographically.

DISCUSSION

Up to the present time, the only significant chemical difference between technetium and rhenium is that technetium forms only a tetrachloride[22] whereas rhenium forms a pentachloride.

The polarographic study of pertechnetate and per-rhenate ions has indicated several

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[16] Jezowska, personal communication.

[17] Hieber and Wagner, *Z. Naturforsch.*, 1958, **13*b***, 339.

[18] Hieber and Braun, *Z. Naturforsch.*, 1959, **14*b***, 132.

[19] Vlček, *Coll. Czech. Chem. Comm.*, 1959, **24**, 1748.

[20] Page and Wilkinson, *J. Amer. Chem. Soc.*, 1952, **74**, 6149.

[21] Abel, Hargreaves, and Wilkinson, *J.*, 1958, 3149.

[22] Knox, Tyree, Srivastava, Norman, Bassett, and Holloway, *J. Amer. Chem. Soc.*, 1957, **79**, 3358.

important differences in behaviour, at least one of which may have important preparative consequences.

In 2M-potassium chloride the elements behave similarly, the only noticeable difference being that pertechnetate is reduced at a potential which is about 0·4 v less negative than that required to reduce per-rhenate, thus indicating that Tc^{VII} is more easily reduced than Re^{VII} as might be expected.

We are unable to suggest why such a marked difference occurs between the elements in 4M-perchloric acid.

In 4M-hydrochloric acid the main difference between the elements is that technetium shows the intermediate 6+ state, which has not previously been shown unambiguously to be exhibited by the element.

In 0·1M-potassium hydroxide, rhenium is reduced to the rhenide ion which agrees with the known chemical evidence that rhenides can be prepared by reduction of per-rhenate in alkali solutions.[23] The fact that pertechnetate does not reduce beyond Tc^{IV} suggests that technides may be more difficult to prepare than rhenides.

The results obtained in 0·1M-potassium cyanide are most interesting. Although the waves for per-rhenate were very poor, it seems possible that Re^{VII} is first reduced to Re^{V} and then to Re^{+1}. This would be in agreement with the known chemical behaviour of rhenium. If potassium per-rhenate is reduced with hydrazine hydrate in the presence of potassium cyanide, the compound $K_3[Re^{V}O_2(CN)_4]$ is obtained,[16] which in solution may be $K_3[Re(OH)_4(CN)_4]$. The tendency for cyanide to stabilise octaco-ordination of Re^{V} is demonstrated by the preparation of potassium octacyanorhenate(V).[9] Both compounds are reduced to Re^{+1} in potassium cyanide medium.

Technetium in contrast shows a single wave. If pertechnetate is unaltered in potassium cyanide, then the reduction corresponds to three electrons, *i.e.*, $Tc^{VII} \longrightarrow Tc^{IV}$. Technetium is in such a position in the Periodic Table that it is difficult to predict on chemical grounds alone whether it would form an octaco-ordinate or a hexaco-ordinate complex cyanide.

In view of the polarographic results, it seems more likely that a cyanide of the type $K_2Tc(CN)_6$ will be found. This point is being pursued on the preparative scale.

Analytical Procedures for Technetium.—There is no very satisfactory analytical method for technetium on the micro-scale. Nitron pertechnetate and tetraphenylarsonium pertechnetate are both more soluble than the corresponding rhenium compounds and the gravimetric method is not very satisfactory for determinations on 1—5 mg. of technetium. It appears from the present work that technetium can be determined easily by polarography.

Technetium compounds can be easily oxidised to Tc^{VII} and after removal of excess of oxidising agent the solution can be polarographed in the most convenient supporting electrolyte.

For accurate determination the wave in 0·1M-potassium cyanide and the first wave in 0·1M-potassium hydroxide are probably best because they are well defined. For merely detecting technetium the wave in 2M-potassium chloride is undoubtedly the most sensitive.

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INORGANIC CHEMISTRY RESEARCH LABORATORIES,
IMPERIAL COLLEGE, LONDON, S.W.7.

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