QUARTERLY REVIEWS

AN OUTLINE OF TECHNETIUM CHEMISTRY

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The first synthetic element was discovered in 1937 when Perrier and Segré[1] showed that a radioactive material produced by irradiating molybdenum sheet with deuterons behaved in such a way that it could only have been element 43. They have since named the element "technetium" from the Greek word meaning artificial.[2]

Much of the work on technetium has been carried out at the Oak Ridge National Laboratory by Boyd and his collaborators who have recently produced technetium in kilogramme quantities. It is reasonable to assume that the element will soon be as readily available and at no greater cost than the less-common platinum metals.

The subject has been reviewed by Tribalat[3] and more recently by Anders[4] and by Boyd.[5] A considerable amount of new information has appeared meanwhile and is incorporated in the present Review. The reader may find it useful to refer to the companion Review on rhenium[6] to appreciate the close resemblance between the two elements.

The Natural Occurrence of Technetium.—There have been several claims to the discovery of element 43 in nature, the best known being that of Noddack *et al.* who purported to have found it at the same time as they discovered rhenium.[7] Subsequently, as knowledge of rhenium and its chemistry developed rapidly, no more was heard of element 43, which had been named "masurium" by the claimants, and its existence remained in doubt until its synthesis by Perrier and Segré.

It was quickly realised that with the exception of technetium-98 the isotopes were all too short lived for any primordial technetium to be

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[1] Perrier and Segré, *J. Chem. Phys.*, 1937, **5**, 712.

[2] Perrier and Segré, *Nature*, 1947, **159**, 24.

[3] Tribalat, "Rhenium et Technetium," 1957, Gauthier-Villars, Paris.

[4] Anders, *Ann. Rev. Nuclear Sci.*, 1959, **9**, 203.

[5] Boyd, *J. Chem. Edw.*, 1959, **36**, 7.

[6] Woolf, *Quart. Rev.*, 1961, **15**, 372.

[7] Noddack, Tacke, and Berg, *Naturwiss.*, 1925, **13**, 567.

detectable today. The half life of technetium-98 was not known and several investigators[8, 9] claimed to have detected it in Nature by using neutron activation analysis techniques and observing an activity with a 6-hr. half life which was taken to be technetium-99m. A later search for natural technetium failed,[10] and since the half life of technetium-98, determined at a later date, is about 10^6 yr., the occurrence of primordial technetium is very unlikely.

Natural uranium undergoes spontaneous fission to a small extent and the technetium-99 formed as a fission product has been detected.[11] It has also been reported that technetium lines can be observed in the spectra of certain stars.[12]

Isotopes of Technetium.—Perrier and Segré discovered the isotopes technetium-95 and -97, which have half lives of 60 days and 90 days, respectively. Many other isotopes have been made since that time, the more important of which are listed in Table 1.

TABLE 1. *Isotopes of technetium.*

Isotope	Preparation	Half-life		Decay*	Ref.
^{93}Tc	^{92}Mo (p, γ) ^{93}Tc	^{93m}Tc	43·5 min.	i.t.	13, 14
	^{92}Mo (α, n) ^{93}Tc	^{93g}Tc	2·8 hr.	K	15
^{94}Tc	^{94}Mo $(d, 2n)$ ^{94}Tc		52·5 min.	β^+, K, γ	14, 16, 17
	^{94}Mo (p, n) ^{94}Tc				
^{95}Tc	^{95}Mo (p, n) ^{95}Tc	^{95m}Tc	60 days	K, 3% i.t.	17
	^{92}Mo (α, p) ^{95}Tc	^{95g}Tc	20 hr.	K, γ	18
^{96}Tc	^{95}Mo (p, γ) ^{96}Tc	^{96m}Tc	51·5 min.	i.t.	17
	^{93}Nb (α, n) ^{96}Tc	^{96g}Tc	4·3 days	K	18
^{97}Tc	^{96}Ru (n, γ) ^{97}Ru ^{97}Tc	^{97m}Tc	90 days	i.t.	18, 19
	^{97}Mo $(d, 2n)$ ^{97}Tc	^{97}Tc	$2{\cdot}6 \times 10^6$ yr.	K	20
^{98}Tc	^{98}Mo (p, n) ^{98}Tc		2×10^6 yr.	?	21, 22
^{99}Tc	^{98}Mo (n, γ) ^{99}Mo ^{99}Tc	^{99m}Tc	5·9 hr.		23—27
	fission of U (6·2%)	^{99g}Tc	$2{\cdot}12 \times 10^5$ yr.	β^-	
^{100}Tc	^{100}Mo (p, n) ^{100}Tc		15·8 sec.	?	28, 29
	^{99}Tc (n, γ) ^{100}Tc				
^{101}Tc	^{100}Mo (α, n) ^{101}Tc		15 min.	β, γ	30

* K = K electron capture. i.t. = internal rearrangement. m = metastable state. g = ground state.

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[8] Herr, *Z. Naturforsch.*, 1954, **9A**, 907.
[9] Alperovitch and Miller, *Nature*, 1955, **176**, 299.
[10] Boyd and Larson, *J. Chem. Phys.*, 1956, **24**, 222.
[11] Kenna and Kuroda, *J. Inorg. Nuclear Chem.*, 1962, **23**, 143.
[12] Merrill, *Astrophys. J.*, 1952, **116**, 21.
[13] Easterday and Medicus, *Phys. Rev.*, 1953, **89**, 752.
[14] Motta and Boyd, *Phys. Rev.*, 1948, **74**, 220.
[15] Levi and Papineau, *Compt. rend.*, 1954, **239**, 2313.
[16] Marmier, *Phys. Rev.*, 1948, **73**, 1208.
[17] Medicus, Prieswerk, and Scherrer, *Helv. Phys. Acta*, 1950, **23**, 299.
[18] Motta and Boyd, *Phys. Rev.*, 1948, **74**, 344.

The Laboratory Handling of Technetium.—The handling of technetium (^{99}Tc) on a small scale ($<\frac{1}{2}$ g.) does not present a serious health hazard provided elementary precautions are taken. This isotope emits only weak β radiation ($\beta_{max} = 0{\cdot}3$ Mev), which is effectively stopped by ordinary laboratory glassware, and there is no associated γ radiation. The essential requirements for safe handling are a well-ventilated box or cupboard, a simple means of monitoring the working area and the rigorous avoidance of all operations which might allow fumes or dust to escape to the atmosphere.

Standard quantitative techniques on the semimicro-scale are easily adapted for work with technetium, for example, it is convenient to evaporate solutions under infrared lamps; to safeguard against loss by spraying, a beaker is inverted over the vessel.

These remarks should suffice to show that handling a weak β emitter is a very much easier matter than handling an α emitter such as polonium, which requires the full resources of a radiochemical laboratory.[31]

The Isolation and Purification of Technetium.—Early samples of technetium were prepared by deuteron or neutron irradiation of molybdenum, and separations were worked out by using rhenium and platinum as carriers. Technetium is now almost wholly obtained from fission product wastes but many of the early methods of separation are still used.

The first weighable amounts of technetium were produced by the neutron irradiation of 5·7 kg. of molybdenum powder in a nuclear reactor.[32] The technetium could be readily separated from the bulk of the molybdenum by dissolving the metal in concentrated sulphuric acid and distilling over the volatile heptaoxide. Technetium heptasulphide was precipitated from the distillate, platinum disulphide being used as a carrier. After the precipitate had been dissolved in ammoniacal hydrogen peroxide the technetium heptaoxide was again distilled from sulphuric acid. A separation from the rhenium present as an impurity in the molybdenum powder was obtained by repeating the sulphide precipitation step, this time in hydrochloric acid stronger than 8N. Technetium heptasulphide is not precipitated under these conditions, but rhenium heptasulphide separates from the solution.

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[19] Motta and Boyd, *Phys. Rev.*, 1948, **74**, 344.
[20] Boyd, *Phys. Rev.*, 1954, **95**, 113.
[21] Boyd, Siles, Larson, and Baldock, *Phys. Rev.*, 1955, **99**, 1030.
[22] Katcoff, *Phys. Rev.*, 1955, **99**, 1618.
[23] Seaborg and Segrè, *Phys. Rev.*, 1939, **55**, 808.
[24] Lincoln and Sullivan, *Nat. Nuclear Energy Series, IV*, 1951, **9**, 228.
[25] Motta, Boyd, and Larson, *Phys. Rev.*, 1947, **72**, 1270.
[26] Sullivan, *Nat. Nuclear Energy Series, IV*, 1951, **9**, 783.
[27] Segrè and Wu, *Phys. Rev.*, 1940, **57**, 552.
[28] House, Colligan, Kundu, and Pool, *Phys. Rev.*, 1952, **86**, 654.
[29] Boyd, Larson, and Parker, *Phys. Rev.*, 1952, **86**, 1051.
[30] Boyd and Kettle, *Phys. Rev.*, 1951, **83**, 216.
[31] Bagnall, *Quart. Rev.*, 1957, **11**, 30.
[32] Boyd, Larson, and Motta, Unclassified Document, 1948, A.E.C.D. 2151.

Irradiation of molybdenum is unsuitable for the production of large amounts of technetium and accordingly attention was soon turned to the recovery of technetium from fission products.

Parker, Reed, and Rauch[33] isolated milligramme amounts of technetium from several kilogrammes of uranium metal which had been irradiated in a nuclear reactor. The fuel elements were dissolved in 37% hydrochloric acid and the resulting slurry of uranium tetrachloride was slowly oxidised by hydrogen peroxide and bromine water to uranyl chloride. The element was isolated by a series of sulphide precipitations and distillation of the heptaoxide as described above.

The first gram of technetium was isolated from fission-product waste solutions by precipitating tetraphenylarsonium pertechnetate with tetraphenylarsonium perchlorate as a carrier, dissolving the mixed salts in concentrated sulphuric acid, and electrolysing the solution at platinum electrodes.[34] The black deposit obtained was dissolved in 18N-sulphuric acid, technetium heptaoxide was distilled out of the solution, and the element finally isolated by precipitation of the heptasulphide. In a modification, the mixed precipitate of tetraphenylarsonium pertechnetate and perchlorate was dissolved in alcohol and passed through an anion exchange resin in the chloride form. The pertechnetate and perchlorate ions were strongly absorbed and the expensive tetraphenylarsonium chloride was recovered in the eluent. The technetium was eluted quantitatively from the resin by 2N-sodium hydroxide.

More recently solvent extraction has been used to recover the fission product technetium from the residue remaining after the fluorination of irradiated uranium fuel elements.[35] It was extracted by 0·3M-trilaurylamine in a hydrocarbon diluent and after removal of uranium, neptunium, and nitrate ion it was back-extracted into 4N-sodium hydroxide solution.

Boyd and Larson have made an extensive study of the extraction of the pertechnetate ion into about 70 organic solvents[36–38] including alcohols, esters, ketones, ethers, amines, and hydrocarbons. They found that the presence of an electron-donating oxygen or nitrogen atom in the solvent was essential for extraction. The partitioning species was shown to be the pertechnetate ion, and with technetium concentrations below 10^{-3}M the extraction coefficient was independent of the concentration of technetium.

Boyd and Larson have also studied the solvent extraction of technetium in valency states other than seven.[39] They found that chloride complexes of technetium(v) in 12M-hydrochloric acid were not extracted into ether, but partial extraction ($E_a{}^\circ{\sim}3$) was obtained with 0·1M-trioctyl-

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[33] Parker, Reed, and Rauch, Unclassified Document, 1948, A.E.C.D. 2043.

[34] Cobble, Nelson, Parker, Smith, and Boyd, *J. Amer. Chem. Soc.*, 1952, **74**, 1852.

[35] Coleman, Kappelman, and Weaver, *Nuclear Sci. and Eng.*, 1960, **8**, 507.

[36] Boyd and Larson, Unclassified Document, 1957, ORNL 2386, 26.

[37] Boyd and Larson, Unclassified Document, 1958, ORNL 2384, 5.

[38] Boyd and Larson, *J. Phys. Chem.*, 1960, **64**, 988.

[39] Boyd and Larson, Unclassified Document, 1959, ORNL 2782, 12.

phosphine oxide in cyclohexane. The hexachlorotechnetate(IV) ion, $TcCl_6^{2-}$, was extracted efficiently from 6M-hydrochloric acid by trioctylphosphine oxide in cyclohexane.

Radiochemical techniques have been used to follow the separation of technetium from other elements on the small scale and at tracer level, particularly from molybdenum and rhenium. The coprecipitation of tetraphenylarsonium pertechnetate with perchlorate and perrhenate was studied soon after the war.[40] Tribalat and Beydon[41] extracted tetraphenylarsonium pertechnetate with chloroform from alkaline solutions. On the tracer scale it has been shown that pertechnetate ion is extracted by pyridine from sodium hydroxide solutions with an extraction coefficient of about 800.[42] Later work showed that the extraction coefficient increased with increasing concentrations of sodium hydroxide.[43] It was also shown that technetium in potassium carbonate solutions could be extracted efficiently with ethyl methyl ketone.[43].

Ion-exchange techniques have been used to separate technetium from both rhenium and molybdenum. The methods are all similar in principle and the results are tabulated in Table 2.

Technetium has been separated from molybdenum and rhenium by electrical methods. Polarographic results had shown that pertechnetate

TABLE 2. *Ion exchange separations of technetium from molybdenum and rhenium.*

Separation	Resin (and form)	Eluent	Efficiency	Ref.
TcO_4^- from MoO_4^{2-} (0·5M-HCl)	Anion, Dowex-1 (Cl^-)	(*a*) Mo in 1M-HCl (*b*) Tc in 4M-HNO_3	Quantitative	44
TcO_4^- from MoO_4^{2-} (weakly alkaline)	Amberlite IRA-400 (ClO_4^-)	(*a*) Mo in 10% NaOH (*b*) Tc in 0·5M-NH_4·CNS	Quantitative	45
TcO_4^- from ReO_4^- neutral	Dowex-1 (ClO_4^-)	0·2M-$HClO_4$	Poor	46
TcO_4^- from ReO_4^- neutral	Dowex-2 (SO_4^{2-})	(*a*) Re in 0·1M-$(NH_4)_2SO_4$ + NH_4·CNS in NaOH; pH 8·3 (*b*) Tc by increasing salts to 1M	Moderate	47
TcO_4 from ReO_4^- (1M-HCl)	Amberlite IRA-400 (Cl^-)	(*a*) Re with 5% NH_4·CNS (*b*) Tc with 4M-HNO_3	Quantitative	48

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[40] Parker and Martin, Unclassified Document, 1950, ORNL 870, 47.
[41] Tribalat and Beydon, *Analyt. Chim. Acta*, 1953, **8**, 22.
[42] Goishi and Libby, *J. Amer. Chem. Soc.*, 1952, **74**, 6109.
[43] Rimshaw and Malling, *Analyt. Chem.*, 1961, **33**, 751.
[44] Huffman, Oswalt, and Williams, *J. Inorg. Nuclear Chem.*, 1956, **3**, 49.
[45] Hall and Johns, *J. Amer. Chem. Soc.*, 1953, **75**, 5787.
[46] Sen Sarma, Anders, and Miller, *J. Phys. Chem.*, 1959, **63**, 559.
[47] Atterbury and Boyd, *J. Amer. Chem. Soc.*, 1950, **72**, 4805.
[48] Pirs and Magee, *Talanta*, 1961, **8**, 395.

ion could be reduced in sodium hydroxide solution but that perrhenate and molybdate ions were not. Electrolysis of an alkaline solution at a controlled potential produced a deposit of technetium dioxide whilst the rhenium and molybdenum remained in solution.[49]

Carvallo has shown that technetium, molybdenum, and rhenium can be separated by electrophoresis techniques after reduction to lower valency states.[50] The best results were obtained when the electrolyte consisted of hydrazine sulphate and hydrazine hydrate at pH 9. Separation of the elements was obtained after 90 minutes at a potential of 200 volts.

Chemistry of Technetium

Introduction.—Technetium exhibits valencies ranging from 7 to 0. The commonest states encountered are 7, represented by the heptaoxide and the pertechnetates, and 4, represented by the dioxide, the tetrachloride, and the halogenotechnetates. At the present time each of the other valency states is represented by at least one compound. In this multiplicity of valency states technetium closely resembles its congener rhenium and its neighbour ruthenium. Corresponding technetium and rhenium compounds are often isostructural and are frequently similar in appearance and in physical and chemical properties. Like most of its neighbours in the Periodic Table technetium exhibits co-ordination numbers commonly of 4 or 6, but a co-ordination number of 8 has been recognised in the complex $[Tc(diars)_2Cl_4]^+ClO_4^-$. That technetium is reluctant to attain high co-ordination numbers is strikingly shown by the absence of a heptafluoride.

The oxidation–reduction potentials in acid solution of the three Group VII elements confirm (Fig. 1) the intermediate position of technetium, although the difference between rhenium and technetium is not very great. In practice it seems that only in low oxidation states such as +3 will the chemistry of technetium prove to more closely resemble that of manganese, and the little that is known of technetium(III) agrees with this. Some calculated heats of formation and free energies of technetium compounds have been reported.[51]

Elementary Technetium.—The element has been prepared by hydrogen reduction of the heptasulphide, Tc_2S_7,[52] at 1100° and of ammonium pertechnetate, NH_4TcO_4, at 500—600°.[53] The latter gives very pure metal. From solution the element has been obtained as a bright cathodic deposit on platinum by the electrolysis of ammonium pertechnetate in 2N-sulphuric acid in the presence of a trace of fluoride ion.[54] It is likely that other laboratory preparations of the element will become available in due

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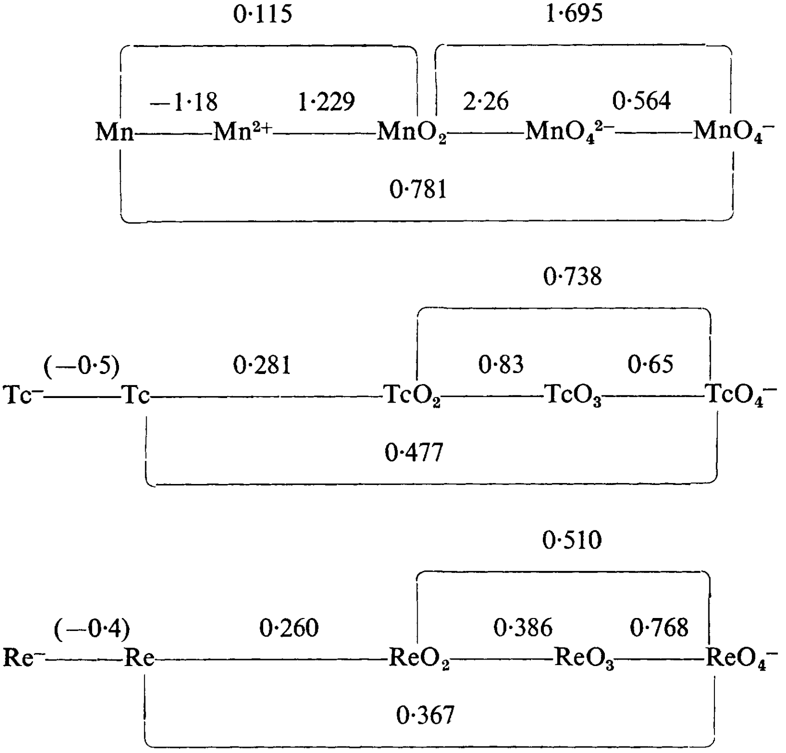
[49] Rogers, *J. Amer. Chem. Soc.*, 1949, **71**, 1507.
[50] Carvallo, Proc. Internat. Conf. Peaceful Uses of Atomic Energy, 1956, **28**, 97.
[51] King and Cobble, *J. Amer. Chem. Soc.*, 1957, **79**, 1559.
[52] Fried, *J. Amer. Chem. Soc.*, 1948, **70**, 442.
[53] Cobble, *J. Amer. Chem. Soc.*, 1952, **74**, 1852.
[54] Motta, Larson, and Boyd, Unclassified Document, 1947, Mon C-99 22.

course; for example, by analogy with rhenium, the hydrogen reduction of ammonium hexachlorotechnetate(IV), $(NH_4)_2TcCl_6$, should give a quite pure preparation at comparatively low temperatures (~300°).

Physical Properties.—The atomic weight (based on natural O = 16) of the element, (^{99}Tc), is 98·8 ± 0·1 determined by the ratio Tc/Tc_2O_7[53] compared with the mass spectrographic value of 98·913.[55] Technetium melts at 2150°[56,57] (rhenium at 3180°). Technetium crystallises in a close-packed hexagonal structure similar to rhenium, ruthenium, and osmium, and the density calculated[58] from the unit cell size is 11·50 g./cm.^{3}. Values[59] for the twelve co-ordinate metallic radii are shown in Table 3.

FIG. 1. *Oxidation–reduction potentials of the manganese group*[51] *(acid solution)*



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[55] Ingram, Hess, and Hayden, *Phys. Rev.*, 1947, **72**, 1269.

[56] Parker, Unclassified Document, 1952, ORNL 1260, 29.

[57] Anderson, Buckley, Helliwell, and Hume-Rothery, *Nature*, 1960, **188**, 48.

[58] Mooney, *Acta Cryst.*, 1948, **1**, 161.

[59] Pauling, "The Nature of the Chemical Bond," 3rd Edn., Oxford University Press, 1960, 403.

TABLE 3. *Metallic radii of technetium and its neighbours (in Å)*[52]

Cr	Mn	Fe
1·276	1·268	1·260
Mo	Tc	Ru
1·386	1·361	1·336
W	Re	Os
1·394	1·393	1·350

Chemical Properties.—The spongy metal tarnishes slowly in air and burns in oxygen. With fluorine the hexafluoride is formed at 400°, and with chlorine at the same temperature a mixture of the hexachloride and tetrachloride is obtained. Technetium dissolves in oxidising acids such as nitric (dilute or concentrated), sulphuric, and aqua regia, but not in hydrochloric acid.[52] Contrary to earlier reports[53] it dissolves in aqueous hydrogen peroxide solutions;[60] the course of this reaction, as with rhenium, is undoubtedly influenced by the state of division of the metal.

Oxides.—Technetium is known to form two oxides, the volatile heptaoxide Tc_2O_7 and the comparatively involatile dioxide TcO_2. Technetium heptaoxide is the only product when the metal is burned in excess of oxygen at 500°.[61,62] The yellow crystalline solid melts at 119·5° to a viscous yellow liquid which is presumably polymeric and could therefore contain six-co-ordinate technetium. The solid is not isostructural with rhenium heptaoxide and is apparently of lower symmetry.[5] Unfortunately, only the unit cell size of rhenium heptaoxide has been reported,[63] so it is not possible to determine whether the different symmetry of the technetium compound really indicates a fundamental change in structure. However, it is interesting to note that although solid technetium heptaoxide conducts electricity and liquid technetium heptaoxide is non-conducting, the reverse holds for rhenium heptaoxide; interesting too, is the large liquid range of technetium heptaoxide compared with that of the rhenium compound. Technetium heptaoxide has a boiling point, estimated from the vapour pressure curve, of 311° ± 2°,[62] a value which has recently been confirmed by direct measurement.[64] It is stable up to the boiling point.[64] The compound is weakly paramagnetic.[65]

Chemically, technetium heptaoxide is a stronger oxidising agent than rhenium heptaoxide. It dissolves readily in water and is also soluble in dioxan, presumably forming a complex.

Several workers have tried to make the trioxide, TcO_3, by reaction between the metal and the heptaoxide[66] (cf. rhenium trioxide) but none

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[60] Colton, Unpublished observation, 1961.
[61] Boyd, Cobble, Nelson, and Smith, *J. Amer. Chem. Soc.*, 1952, **74**, 556.
[62] Smith, Line, and Bell, *J. Amer. Chem. Soc.*, 1952, **74**, 4964.
[63] Wilhelmi, *Acta Chem. Scand.*, 1955, **9**, 1378.
[64] Peacock, Unpublished observation, 1962.
[65] Nelson, Boyd, and Smith, *J. Amer. Chem. Soc.*, 1954, **76**, 348.
[66] Cobble, Smith, and Boyd, *J. Amer. Chem. Soc.*, 1953, **75**, 5777.

has been completely successful, although Fried and Hall[67,68] described a volatile purple oxide $TcO_{3\cdot05}$ from the action of oxygen on technetium metal at 400—1000° (see also refs. 66 and 92).

The black anhydrous dioxide, like rhenium dioxide, has the molybdenum dioxide structure[69]. It sublimes unchanged at temperatures between 900° and 1100°[65] and it is the ultimate product of the decomposition of the heptaoxide. Technetium dioxide has been prepared in a number of ways. The dihydrate can be readily precipitated by the reduction of a pertechnetate solution with zinc and hydrochloric acid[65] (cf. rhenium dioxide), by the hydrolysis of a warm solution of a halogenotechnetate with sodium carbonate or hydrogen carbonate, or by the electrolysis of neutral or alkaline pertechnetate solutions at platinum electrodes.[54] The anhydrous compound, made by dehydrating the hydrated dioxide in a vacuum at 250—500°, has also been prepared directly by the thermal decomposition of ammonium pertechnetate, $NH_4\cdot TcO_4$.[67]

The anhydrous compound is stable to the atmosphere at the ordinary temperature, but it is easily oxidised to the heptaoxide by oxygen and it also interacts with chlorine at 300° to give a technetium(V) oxide chloride.[60] The hydrated oxide is converted into pertechnetate by hydrogen peroxide in alkaline solution, or in neutral solution by cerium(IV) or by bromine water.[70]

Oxyacids and their Salts.—Only one oxyacid of technetium and the corresponding series of salts are known—pertechnetic acid and the pertechnetates. Technetium heptaoxide dissolves in water to form a colourless solution, which on evaporation gives dark red crystals of anhydrous pertechnetic acid, $HTcO_4$.[61] Concentrated solutions of the acid are also red. Pertechnetic acid is a strong acid, and, like perrhenic acid it can be titrated by using indicators such as methyl red.

The colourless pertechnetates closely resemble the perrhenates though they are more soluble in water, *e.g.* the solubility of potassium pertechnetate, $KTcO_4$ (21·3 g./1000 g.),[71] is intermediate between that of potassium perrhenate, $KReO_4$ (11·8 g./1000 g.), and permanganate, $KMnO_4$ (64·0 g./1000 g.). The alkali salts are very stable, and potassium pertechnetate, which undergoes a reversible colour change to yellow at 500°, can be fused at about 540° and sublimed at about 1000° without decomposition.[72]

The pertechnetate ion, like the perrhenate ion, is stable in solution over a very wide range of pH, and so far no direct evidence has been found for the existence of an ion corresponding to the mesoperrhenate ReO_5^{3-} nor for lower states such as TcO_4^{2-} and TcO_4^{3-}, although these are reasonably

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[67] Fried and Hall, "Chemistry of Technetium" 1950; presented at Spring Meeting of Amer. Chem. Soc.

[68] Fried and Hall, *Phys. Rev.*, 1951, **81**, 741.

[69] Magneli and Anderson, *Acta Chem. Scand.*, 1955, **9**, 1378.

[70] Colton, Griffiths, Dalziel, and Wilkinson, *J.*, 1960, 71.

[71] Busey and Bevan, Unclassified Document, 1960, ORNL 2983.

[72] Busey and Larson, Unclassified Document, 1958, ORNL 2584.

well known for rhenium in the solid state. The possible stability of TcO_4^{2-} in aqueous solution has been discussed.[51]

The pertechnetate ion absorbs strongly in the near ultraviolet region. The edge of the 2875 Å peak is very close to the visible region of the spectrum, and evidently only a small disturbance from the tetrahedral symmetry of the TcO_4^- ion is necessary to cause a strong colour, such as is shown by the free acid. It is interesting to note that a persistent reddish-violet colour, resembling that of the free acid, is sometimes found in solid pertechnetates which have been dried under the infrared lamp; indeed a definite absorption band at about 5000 Å was recorded by some of the earlier workers.[33]

The chemistry of potassium pertechnetate has been studied in hydrochloric acid solutions and will be discussed later.

Sulphides.—Technetium forms two sulphides, Tc_2S_7 and TcS_2. These are prepared in analogous ways to those of rhenium which they closely resemble.

Technetium heptasulphide is formed by the action of hydrogen sulphide on a pertechnetate dissolved in 2–4N-hydrochloric acid.[73] The crude material is freed from sulphur by carefully washing it with carbon disulphide. The heptasulphide loses sulphur when heated at moderate temperatures and yields the amorphous disulphide. Crystalline disulphide is made by heating the heptasulphide with sulphur at 1000° for 24 hours in a bomb, the excess of sulphur being sublimed away in a vacuum. Technetium disulphide is isostructural with rhenium disulphide[74] and is thought to have a disordered molybdenum disulphide structure. When heated with either hydrogen or hydrogen sulphide at 1000° the disulphide is reduced to the metal.

Halides and Complex Halides.—The known halides and oxide halides of technetium are listed with those of rhenium in Table 4.

Technetium hexafluoride. Technetium hexafluoride (m.p. 33·4°; b.p. 55·3°), prepared by the action of fluorine on the metal at 400°, is a yellow solid melting to a yellow liquid. The vapour is colourless and monomeric.[75] As in other transition-metal hexafluorides there is a phase transition in the solid marking the change from the cubic high-temperature form to the orthorhombic low-temperature form; for the hexafluoride this change occurs at $-5{\cdot}3°$ (calculated from vapour-pressure measurements, $-4{\cdot}54°$). Vapour-pressure and spectroscopic measurements indicate that under the experimental conditions heptafluoride is not formed. The magnetic moment ($\mu_{\text{calc}} = 0{\cdot}45$ B.M. at 300°K) is very low, and, like rhenium hexafluoride, technetium hexafluoride exhibits peculiar magnetic be-

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[73] Rulfs and Meinke, *J. Amer. Chem. Soc.*, 1952, **74**, 235.

[74] Zachariasen, quoted as private communication in ref. 5.

[75] Selig, Chernik, and Malm, *J. Inorg Nuclear Chem.*, 1961, **19**, 377.

haviour at temperatures below 14°K.[76] The infrared spectrum over the range 600—2000 cm.$^{-1}$ is similar to the spectra of other transition-metal hexafluorides and there is a strong fundamental absorption at 745 cm.$^{-1}$. Upon hydrolysis with sodium hydroxide, technetium hexafluoride yields a black precipitate which dissolves upon addition of dilute hydrogen peroxide; this behaviour is reminiscent of rhenium hexafluoride which disproportionates on hydrolysis to perrhenate and hydrated dioxide.

TABLE 4. *Halides and oxyhalides of technetium and rhenium.*

	Fluorides	Chlorides	Bromides
Tc(VII)	TcO_3F?	TcO_3Cl?	—
Re(VII)	ReF_7, $ReOF_5$, ReO_3F, ReO_2F_3	ReO_3Cl	ReO_3Br
Tc(VI)	TcF_6	$TcCl_6$	
Re(VI)	ReF_6 $ReOF_4$	$ReCl_6$ $ReOCl_4$	$ReOBr_4$
Tc(V)			$TcOBr_3$
Re(V)	ReF_5 $ReOF_3$	$ReCl_5$	$ReBr_5$
Tc(IV)		$TcCl_4$	
Re(IV)	ReF_4		$ReBr_4$
Tc(III)			
Re(III)		Re_2Cl_6	Re_2Br_6

Chlorides. It was reported that chlorine had no action on heated technetium metal, but the chlorination was carried out in a closed static system.[65] It has recently been shown that a stream of chlorine readily reacts with technetium to produce both the hexachloride and the tetrachloride.[77]

Technetium hexachloride is a volatile green compound. It is readily decomposed thermally to the red tetrachloride, and on hydrolysis gives technetium dioxide and the pertechnetate ion according to the usual disproportionation reactions of rhenium(VI) and technetium(VI) compounds:—

$$3Tc(VI) \rightarrow 2Tc(VII) + Tc(IV)$$

Technetium tetrachloride is stable. It can be made by the action of chlorine on the metal and it can be sublimed unchanged in the chlorine stream. It was first prepared, however, by the action of carbon tetrachloride on technetium heptaoxide at 400° in a bomb.[78] Technetium tetrachloride reacts with oxygen to give oxide chlorides of technetium(VII)[79] and it

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[76] Selig and Malm, Personal communication.

[77] Colton, *Nature*, 1962, 193, 872.

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

[79] Colton, 1962, to be published.

dissolves readily in concentrated hydrochloric acid to give the hexachlorotechnate(IV) ion, $TcCl_6^{2-}$.[79] It dissolves in water to give a yellow solution which hydrolyses only slowly[79] (cf. platinum tetrachloride). The magnetic susceptibility of technetium tetrachloride has been measured over a temperature range.[80] It was found to obey the Curie–Weiss law fairly closely with $\mu_{eff} = 3{\cdot}14$ B.M. (25°C) and $\theta = -57°$.

No binary bromides or iodides of technetium have so far been characterised.

Oxide halides. The existence of pertechnyl fluoride, TcO_3F, was suspected from a mass-spectroscopic examination of the products formed from technetium heptaoxide and uranium tetrafluoride.[81] This compound, which has properties intermediate between those of MnO_3F and ReO_3F, has very recently been obtained by the direct fluorination of technetium dioxide.[82]

Pertechnyl chloride, TcO_3Cl, is said to have been prepared by treating potassium pertechnetate dissolved in 18M-sulphuric acid with 12M-hydrochloric acid. The compound was extracted into chloroform, carbon tetrachloride, or hexane.[72] Although its vibrational spectrum was recorded, there is no record of it having been isolated and properly characterised.

Two products which were thought to be oxide chlorides were observed during the reaction between chlorine and technetium dioxide.[65] The first was blue, subliming at 80—90°, and the second was a brown product subliming at 900°. Neither was characterised but it has since been suggested that the brown product was technetium oxide trichloride, $TcOCl_3$.[5] This has recently been confirmed.[60]

The only other oxide halide of technetium which has been definitely characterised is the brown oxide tribromide, $TcOBr_3$, prepared by the action of bromine vapour on technetium dioxide at about 350°.[83] Under similar conditions rhenium gives an oxide tetrabromide, $ReOBr_4$.[84] The technetium compound can be sublimed in a bromine stream at 400°. It hydrolyses in the usual way for compounds of rhenium(V) and technetium(V):

$$3Tc(\text{V}) \rightarrow 2Tc(\text{IV}) + Tc(\text{VII})$$

Complex halides. The pink complex fluoride, potassium hexafluorotechnetate(IV), K_2TcF_6, has been obtained from reaction between the hexachlorotechnetate(IV) and potassium hydrogen difluoride melt.[85] It is isostructural with the hexafluororhenate (K_2GeF_6 structure), but is more stable to water and, like the hexafluororhenate can be recrystallised from aqueous solution. The free acid, as well as other fluorotechnetates, can be obtained from the potassium salt by ion exchange. The sodium and

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[80] Knox and Coffey, *J. Amer. Chem. Soc.*, 1959, **81**, 7.
[81] Sites, Baldock, and Gilpatrick, Unclassified Document, 1952, ORNL 1327.
[82] Selig, 1962, Personal communication.
[83] Colton, 1961, to be published.
[84] Colton, *J.*, 1962, 2078.
[85] Boyd, 1962, Personal communication.

ammonium salts are very soluble; the barium salt, like barium hexafluororhenate,[86] becomes less soluble on ageing. A solid silver salt could not be isolated from solution even by evaporation in the dark; this behaviour resembles that of the corresponding rhenium salt.

Although potassium pertechnetate treated with concentrated hydrochloric acid yields the hexachlorotechnetate, K_2TcCl_6;[87] this salt is more conveniently prepared by the action of concentrated hydrochloric acid and potassium iodide on potassium or ammonium pertechnetate,[65,88] In the latter reaction the oxygenated species $K_4[Tc_2OCl_{10}]$ is obtained as an intermediate[83] and is converted into the hexachlorotechnetate by further treatment with hydrochloric acid.

Potassium hexachlorotechnetate(IV) forms golden yellow octahedra and is isostructural with the corresponding rhenate and platinate. The magnetic moment of the solid is 4·8 B.M.;[65] two values have been obtained in solution: 4·05 B.M. by the Gouy method[88] and 3·83 B.M.[89] by Evans's nuclear magnetic resonance method.[90]

The hexachlorotechnetate(IV) ion is not so stable in solution as its rhenium analogue. Thus the silver salt cannot be prepared by the reaction of silver nitrate with a neutral solution of the potassium salt because of rapid hydrolysis, although this is the method used for making silver hexachlororhenate(IV).[65] Even qualitative observation shows that potassium hexachlorotechnetate(IV) is hydrolysed in dilute hydrochloric acid; more detailed study[87] has indicated that the potassium salt is unstable in 1M-hydrochloric acid, decomposing to an oxygenated species.

Potassium hexabromotechnetate(IV), K_2TcBr_6, can be prepared quantitatively from the corresponding chloride by evaporation with hydrobromic acid.[88] The compound forms dark red or black crystals which have a face-centred cubic structure. The magnetic moment has been measured in solution only: 3·94 B.M. was the value obtained by the Gouy method[88] and 3·5 B.M. by the nuclear magnetic resonance method.[89]

Potassium hexaiodotechnetate(IV), K_2TcI_6, is made by evaporating the corresponding chloride or bromide with hydriodic acid. The shiny black crystals are monoclinic,[88] but the structure is probably a modification of the potassium hexachloroplatinate(IV) type. The magnetic moment in hydriodic acid solution was found to be 4·14 B.M. by the Gouy method.[88]

The first crystals separating during the reduction of potassium pertechnetate by potassium iodide in hydrochloric acid are red.[83] When digested with large quantites of hydrochloric acid these dissolve to give a reddish solution, which slowly becomes light yellow and deposits crystals of the hexachlorotechnetate on cooling. The red crystals are a binuclear complex $K_4[Tc_2OCl_{10}]$, analogous to the well-known rhenium and ruthenium

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[86] Peacock, *J.*, 1956, 1291.
[87] Busey, Unclassified Document, 1959, ORNL 2782.
[88] Dalziel, Gill, Nyholm, and Peacock, *J.*, 1958, 4012.
[89] Colton, 1960, Unpublished observations.
[90] Evans, *J.*, 1959, 2003.

compounds.[91,92] The crystals are stable in the atmosphere, but hydrolyse rapidly in water, the technetium being deposited as dioxide.[83]

Chloro-complexes of technetium(v) have been observed in solution.[87] In 12M-hydrochloric acid, potassium pertechnetate is reduced to technetium(v) directly by chloride ion without the formation of intermediates. It has been suggested that the oxyion $TcOCl_4^-$ is formed. The absorption spectrum of the complex shows bands at 2925 and 2300 Å (ϵ = 4700 and 10,400, respectively). Further reduction to $TcCl_6^{2-}$ occurs only slowly. The technetium(v) complex, while stable in 3M-hydrochloric acid, disproportionates to pertechnetate and the hydrolysis products of the hexachlorotechnetate(IV) ion in 1M-hydrochloric acid.

A different technetium(v) species is produced when a solution of potassium hexachlorotechnetate in 12M-hydrochloric acid is exposed to sunlight.[87] This complex shows a band at 3260 Å (ϵ = 7800).

It is evident that the reduction of pertechnetate ion by and in hydrochloric acid solutions is a complicated process. The exact nature of the technetium(v) species remains to be resolved, and the relation between them and the binuclear ion $Tc_2OCl_{10}^{4-}$, which is not formed in pure hydrochloric acid solutions, requires investigation.

Complex Compounds.—Apart from the halogenotechnetates and certain reactions of analytical interest, the chemistry of technetium complexes has received little attention.

Hydrated technetium dioxide, $TcO_2,2H_2O$, dissolves in alkali cyanides to give an anion believed to be $[Tc^{IV}(OH)_3(CN)_4]^{3-}$ which was isolated as the dark brown thallium salt.[93] Under similar conditions rhenium gives $[Re^{V}(OH)_4(CN)_4]^{3-}$.[94] Polarographic studies[70] suggest that technetium should form quadrivalent rather than quinquevalent cyanide complexes, so that the $[Tc(OH)_3(CN)_4]^{3-}$ ion merits further study on account of both oxidation state and co-ordination number. The complex oxycyanide was reduced by potassium amalgam to the technetium(I) complex cyanide, $K_5Tc(CN)_6$,[93] similar to and isostructural with the corresponding manganese and rhenium compounds.

By using *o*-phenylenebisdimethylarsine (L) as the ligand, complexes of the types $[Tc^{II}Cl_2L_2]$, $[Tc^{III}Cl_2L_2]Cl$, and $[Tc^{V}Cl_4L_2]ClO_4$ have been prepared.[95,96] The first two are so far the only isolated and characterised compounds of technetium in the valency states 2 and 3. The technetium(v) compound affords the only example so far of eight co-ordination for technetium. The compounds are isostructural with the corresponding rhenium compounds[97] which they closely resemble.

[91] Croft, *Austral. J. Chem.*, 1956, **9**, 184.
[92] Mathieson, Mellor, and Stephens, *Acta Cryst.*, 1952, **5**, 185.
[93] How and Schwochau, *Angew. Chem.*, 1961, **73**, 492.
[94] Trzebiatowska and Danowska, *Z. phys. Chem.*, 1959, **212**, 29.
[95] Fergusson and Nyholm, *Nature*, 1959, **183**, 1039.
[96] Fergusson and Nyholm, *Chem. and Ind.*, 1960, 347.
[97] Curtis, Fergusson, and Nyholm, *Chem. and Ind.*, 1958, 625.

Organometallic compounds of technetium have only recently been prepared. Technetium tetrachloride reacts with sodium cyclopentadienide in tetrahydrofuran to give a reddish purple solution which on treatment at 50° with sodium borohydride yields air-sensitive yellow crystals of composition $Tc(C_5H_5)_2$.[98] The infrared spectrum of this compound resembles that of $(C_5H_5)_2ReH$[99,100] but the characteristic stretching frequency of a metal–hydrogen bond is absent. Molecular weight determinations indicate a dimer and nuclear magnetic resonance spectroscopy shows the compound to be diamagnetic and confirms the absence of a metal–hydrogen bond.[98] Chemical evidence suggests that the bonding between the rings and the metal ion resembles that in $(C_5H_5)_2ReH$. There does not appear to be any similarity between the bonding in the technetium compound and that in the paramagnetic manganese cyclopentadienide[101] and it is probable that the molecule has a metal–metal bond.

The dibenzenetechnetium cation $[(C_6H_6)_2Tc]^+$ is said to be formed in trace amounts by the neutron irradiation of dibenzenemolybdenum.[102]

Technetium carbonyl has been prepared by the action of carbon monoxide on technetium heptaoxide at 220—275° and 400 atmospheres pressure.[103,104] The molecular weight is twice the formula weight, that is $Tc_2(CO)_{10}$, and the presence of a metal–metal bond similar to those in manganese and rhenium carbonyls has been established from the infrared absorption spectrum. The colourless diamagnetic compound sublimes at moderate temperatures in a vacuum and slowly decomposes in the atmosphere.

Technetium carbonyl slowly reacts with iodine to form the dimeric carbonyl halide $[Tc(CO)_4I]_2$, but when treated with iodine under a pressure of 50 atmospheres of carbon monoxide the monomeric pentacarbonyl iodide $Tc(CO)_5I$ is formed.

When ammonium perrhenate solution labelled with technetium-99 is reduced by potassium in ethylenediamine the technetium, like the rhenium, is converted into a complex hydride.[105] By analogy with the rhenium compound the formula of the hydride was thought to be $KTcH_4,2H_2O$. The available evidence suggests that this hydride ion is less stable than the rhenium analogue.

The more important compounds of technetium are shown in Table 5.

Polarographic Studies.—Polarographic studies of technetium compounds in various supporting electrolytes have been described and some differences between technetium and rhenium have been found.

[98] Huggins and Kaesz, *J. Amer. Chem. Soc.*, 1961, **83**, 4474.
[99] Wilkinson and Birmingham, *J. Amer. Chem. Soc.*, 1955, **77**, 3421.
[100] Green, Pratt, and Wilkinson, *J.*, 1958, 3916.
[101] Wilkinson, Cotton, and Birmingham, *J. Inorg. Nuclear Chem.*, 1956, **2**, 95.
[102] Baumgartner, Fischer, and Zahn, *Naturwiss.*, 1961, **48**, 478.
[103] Hileman, Huggins, and Kaesz, *J. Amer. Chem. Soc.*, 1961, **83**, 2953.
[104] Hieber and Herget, *Angew. Chem.*, 1961, **73**, 579.
[105] Floss and Grosse, *J. Inorg. Nuclear Chem.*, 1961, **16**, 44.

Potassium pertechnetate in 2M-potassium chloride shows the same apparently eight-electron reduction as rhenium to give the "technide" ion.[70] Little is known about the constitution of this ion although a technide has been isolated.[105] The present position regarding the "rhenides" is chaotic[6] and until the rhenides have been properly characterised it is not worth speculating on the structure of the technide.

Surprisingly, potassium pertechnetate shows no reduction wave in 4M-perchloric acid although the perrhenate gives a good wave, corresponding to a three-electron reduction to rhenium(IV).[106,107] Similarly, in 4M-hydrochloric acid perrhenate ion is reduced to rhenium(IV) in a single wave[106,107] but technetium shows evidence of an intermediate technetium(VI) state.[70]

TABLE 5. *Compounds of technetium.*

Tc(VII)	Tc_2O_7, $HTcO_4$, $MTcO_4$ (M = K^+, NH_4^+, Cs^+, Ph_4As^+, etc.) Tc_2S_7, TcO_3F
Tc(VI)	TcF_6, $TcCl_6$
Tc(V)	$TcOBr_3$, $[TcL_2Cl_4]ClO_4$ (L = *o*-phenylenebisdimethylarsine)
Tc(IV)	TcO_2, TcS_2, $TcCl_4$ K_2TcX_6 (X = F, Cl, Br, I), $K_4[Tc_2OCl_{10}]$
Tc(III)	$[TcL_2Cl_2]Cl$
Tc(II)	$[TcL_2Cl_2]$
Tc(I)	$Tc(CO)_5X$, $[Tc(CO)_4X]_2$ (X = Cl, Br, I)
Tc(0)	$Tc_2(CO)_{10}$

In 0·1M-potassium cyanide potassium pertechnetate gives only one wave corresponding to a three-electron reduction to technetium(IV).[70] Perrhenate gives two waves; the first is to rhenium(V) and the second corresponds to reduction to rhenium(I).[70] These results agree with the chemical behaviour of the elements; thus no technetium(V) cyanide has yet been prepared. Green technetium(III) solutions have been prepared by the controlled potential electrolysis of pertechnetate solution at pH 7·0 in a phosphate buffer. The solutions are unstable and readily oxidise to technetium(IV).[108]

Analysis.—*Radioactivity.* The earliest method of determining technetium was by means of its radioactivity.[1] The method is sensitive, as the specific activity of technetium-99 is 37,800 disintegrations/min./μg., but difficulties associated with measurements of low-energy β particles arise due to self absorption in the specimens. Hence the method is not the best for weighable amounts of technetium.

Gravimetric methods. These usually depend on the formation of sparingly soluble pertechnetates. The two most common precipitants are the tetraphenylarsonium cation and nitron.[40] Unfortunately neither is

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[106] Lingane, *J. Amer. Chem. Soc.*, 1942, **64**, 1001.
[107] Rulfs and Elving, *J. Amer. Chem. Soc.*, 1951, **73**, 3281.
[108] Thomason, Unclassified Document, 1958, ORNL 2453, 7.

specific, and many anions, including perrhenate, nitrate, iodide, and bromide, interfere. Technetium can be determined by precipitating the sulphide under carefully controlled conditions.[73]

Spectrophotometric methods. The simplest is the measurement of the intensity of the characteristic peaks of the pertechnetate ion which occur at 2460 and 2890 Å.[72] This method has been used for the simultaneous estimation of technetium and rhenium.[109] Other methods involve the formation of technetium complexes with thiocyanates,[110] furil-α-dioxime,[111] toluene-3,4-dithiol,[112] and thioglycollic acid.[113] The spectrophotometric methods are very sensitive—about 10 μg. of the element can be easily estimated—and are therefore to be recommended on the grounds of safety. Several other reagents, such as potassium xanthate, dimethylglyoxime, and thiourea, give colour reactions with technetium ions under special conditions, and it is possible that from these other, more specific, quantitative methods may be developed.[114]

Other methods. Traces of technetium may be determined polarographically,[70,108] but the most sensitive method for very small amounts is neutron activation analysis. Technetium-99 has a moderate cross section for neutron capture (20 barns) to give the 15·8 sec. technetium-100.[115] However, the method is only convenient if a reactor or neutron source is available.

The Future.—Technetium is a relatively stable fission product, and the working up of the quantities present in spent fuel elements from nuclear reactors is a matter of economics rather than of the scarcity of the element itself. No recent figure of the amount of technetium present in the waste from such reactors is available, but there is little doubt that kilogramme or larger quantities could be isolated if the demand existed.

The uses of technetium will be limited by its radioactivity. The pertechnetate ion has been shown to be an efficient anticorrosion agent in solution, in contrast to perrhenate,[116] and the concentration of pertechnetate required is sufficiently low ($<10^{-4}$ molar) for the radioactivity hazard to be small. Alloys of technetium, except those containing other fission products and uranium, have been little studied, but already they have been considered as superconductors.[117] A start has been made on the organometallic chemistry of the element, and this field could well produce potential catalysts.

We thank Dr. A. A. Woolf for a thorough reading of the manuscript.

[109] Wolkowitz, Unclassified Document, 1955, ORNL 1880, 4.
[110] Crouthamel, *Analyt. Chem.*, 1957, **29**, 1756.
[111] Colton and Morley, *U.K.A.E.A. Report*, 1961, AERE R 3746.
[112] Miller and Thomason, *Analyt. Chem.*, 1961, **33**, 404.
[113] Miller and Thomason, *Analyt. Chem.*, 1960, **32**, 1429.
[114] Jasmi, Magee, and Wilson, *Talanta*, 1959, **2**, 93.
[115] Boyd and Larson, *J. Phys. Chem.*, 1956, **60**, 707.
[116] Cartledge, *J. Phys. Chem.*, 1957, **61**, 973.
[117] Buckel, *Metallurgy*, 1959, **13**, 814.