AN OUTLINE OF RHENIUM CHEMISTRY

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RHENIUM is the rarest of the naturally occurring elements. Its average concentration in the earth's crust (0·001 part per million) is of the same order of magnitude as that of some of the platinum metals, but it does not occur as the element or as a distinct mineral species. Ores or residues are considered rich in rhenium when they contain 10—100 p.p.m. though one really exceptional ore has been found which contained 3000 p.p.m. In spite of, or perhaps even because of, its rarity, rhenium is by no means one of the less familiar elements and the extent of its chemistry can only be outlined here. However, rhenium chemistry has been so well documented since its early days that the reader can consult the latest books for details,[1-3] and allow the Reviewer a bias towards the more recent work not reported therein.

Discovery, Production and Preparation of the Metal

The discovery of rhenium seems conventional when viewed in retrospect. Its existence as dvi-manganese was predicted by Mendeléev. It may have been discovered in the last century, but adequate confirmation had to await Moseley's law which unequivocally related the X-ray spectra of elements with their atomic numbers. It was not until 1925, however, that the X-ray spectrum expected for element 75 was found by the Noddacks, together with Berg, in concentrates from platinum minerals and by Loring and Druce in manganese compounds. Heyrovsky and Dolejšek also confirmed the presence of rhenium in commercial manganese salts by the then novel technique of polarography. By 1928 the Noddacks had laboriously isolated the first gram of rhenium. Feit achieved technical scale preparation (100—200 kg./annum) in the 1930's from molybdenite residues recovered from copper schists. Nowadays most rhenium is recovered as a by-product in the manufacture of molybdenum and world production is probably in the region of 5 tonnes/annum.

The flue dusts obtained from molybdenum concentrates are enriched in rhenium because of the volatility of rhenium heptaoxide. The rhenium contained in this dust can be extracted with water containing an oxidising agent; alternatively, the rhenium in the concentrates can be solubilised without volatilisation by heating them with lime at 600°. Calcium perrhenate is readily leached out with water from the insoluble calcium molybdate. Direct solution is possible by leaching at low temperatures

[1] Druce, "Rhenium", Cambridge University Press, Cambridge, 1948.
[2] Tribalat, "Rhénium et Technétium", Gauthier-Villars, Paris, 1957.
[3] Lebedev, "Renii", Moscow, 1960.

under pressure (170—200° and 50 atmospheres). The rhenium in solution can then be recovered by (a) precipitation of potassium per-rhenate or rhenium heptasulphide, (b) ion exchange[4] or adsorption[5] (this is particularly effective for separating molybdenum from rhenium because their highest-valency state ions carry different charges, and by altering the conditions can be made anionic or cationic), (c) electrodeposition from acid solutions, (d) cementation on to iron sponge in acid solution,[6] or (e) solvent extraction from acid or alkali solution.[7]

In most processes the impure product can be converted into potassium per-rhenate which is easily purified by recrystallisation. Originally the metal was produced by reducing this salt with hydrogen at 1000° but the product was always contaminated with potassium. Impure rhenium can be purified by conversion into the pentachloride with chlorine, hydrolysing the pentachloride to rhenium dioxide, and reducing the last.[8] On a small scale it is more convenient to convert potassium per-rhenate into the ammonium salt on ion-exchange resins and then to reduce this salt to a purer rhenium.[9] The reduction temperature can be lowered considerably by using a hydrogen pressure of 50 atmospheres.

Thermal decomposition of rhenium chlorides and carbonyls is used mainly to coat other metals with rhenium. The relative instability of rhenium iodides precludes a continuous van Arkel–de Boer method of purification.[10] Electrolysis of per-rhenates in aqueous solution does not yield pure rhenium;[11] the electrodeposit always contains some oxide and it is usual to anneal in hydrogen at 1000° to achieve permanent coatings.[12] Rhenium is the highest-melting metal (3180°), next to tungsten, and has a density of 21·04. The natural element consists of only two isotopes, ^{187}Re and ^{185}Re, but nine other radioisotopes are known.

The Oxygen Compounds of Rhenium

Rhenium Heptaoxide.—This results when the metal is heated in air or oxygen. The oxidation proceeds through intermediary lower oxides since one can observe the red trioxide on some faces of a single metal crystal at lower oxygen pressures,[13] and conversely the dioxide can be isolated by hydrogenating the heptaoxide at about 300°. The peroxide (Re_2O_8), once claimed, seems to have been a fine spray of per-rhenic acid caused by

[4] Meloche and Preuss, *Analyt. Chem.*, 1954, **26**, 1911; Ryabchikov and Borisova, *Zhur. anal. Khim.*, 1958, **13**, 155, 492.
[5] Alexander, *J. Amer. Chem. Soc.*, 1949, **71**, 3043; Galyaeva, Zimakov, and Rudenko, *Tsvetnye Metally*, 1959, (5), 73.
[6] Kovyrshin and Appolonov, *Tsvetnye Metally*, 1957, (8), 67.
[7] Tribalat, *Ann. Chim.*, 1953, **8**, 642; Kertes and Beck, *J.*, 1961, 1921.
[8] Rosenbaum, Runck, and Campbell, *J. Electrochem. Soc.*, 1956, **103**, 518.
[9] Woolf, *J. Less-Common Metals*, 1959, **1**, 420.
[10] Woolf, *J. Inorg. Nuclear Chem.*, 1958, **7**, 291.
[11] Lundell and Knowles, *J. Res. Nat. Bur. Stand.*, 1937, **18**, 629.
[12] Levi and Espersen, *Phys. Rev.*, 1950, **78**, 231.
[13] Reviewer's unpublished observation.

traces of moisture.[2] The difficulty of collecting the heptaoxide from a flowing gas necessitates oxidation in a static atmosphere, and in such a system the formation of the heptaoxide is a convenient way to purify and separate rhenium.[10]

The melting and boiling points, calculated from vapour-pressure measurements[14] since the solid sublimes, are $300 \cdot 3°$ and $360 \cdot 3°$. In this respect it closely resembles the neighbouring osmium tetraoxide rather than tungsten trioxide. Unlike osmium tetraoxide it is reported to be soluble in ethers, alcohols, and amines without being reduced.

Per-rhenic Acid.—The acid is formed when the heptaoxide dissolves in water. Solutions of the acid can also be prepared by dissolving the metal powder in hydrogen peroxide but with the consolidated metal this oxidation is too slow to be practicable. Anodic oxidation in alkali hydroxide solution[13] followed by removal of the alkali ions on a cation-exchange resin is satisfactory. The acid is strong, as can be demonstrated qualitatively by the behaviour of its salts on ion-exchange resins, the pH of its aqueous solutions, and the attack on metals, metal oxides, hydroxides, and carbonates. Quantitatively the dissociation constant has been determined by observing how the optical absorption of the acid varies with concentration.[15]

The first dissociation constants of perchloric, permanganic, per-rhenic, and periodic acids are 10^7, 400, 40, and $0 \cdot 02$ respectively (the perchloric constant is an estimate). Pauling[16] has suggested an empirical correlation between the strength of an acid and its structure. For an acid $XO_m(OH)_n$ the constants are $\sim 10^{-2}$, $\sim 10^5$, and $\sim 10^8$ for $m = 1$, 2, or 3, respectively. The ortho-acid, H_5IO_6, which can be isolated from aqueous solution, has the acidity expected of an acid with $m = 1$, but the rhenium acid with $m = 2$, which would have the acidity found experimentally, has never been isolated although its salts exist:[17]

$$ReO_4^- + 2OH^- \rightleftharpoons [ReO_4(OH)_2] \rightleftharpoons ReO_5^{3-} + H_2O$$
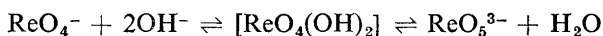
Neither a hydrate nor the anhydrous acid can be obtained from per-rhenic acid solutions. The colourless dilute solution becomes yellow-green on evaporation and additional lines, presumably of the undissociated acid, appear in the Raman spectrum. Further evaporation, which leads to volatilisation of the heptaoxide, has been employed for analytical separation, sulphuric acid being added to raise the distillation temperature.[18]

The per-rhenates resemble the perchlorates in their aqueous solubilities. (There is no corresponding resemblance in organic solvents.) The sodium salts are about a hundred times more soluble than the potassium salts, and

[14] Smith, Line, and Bull, *J. Amer. Chem. Soc.*, 1953, **74**, 4964.
[15] Bailey, Carrington, Lott, and Symons, *J.*, 1960, 290.
[16] Pauling, "The Nature of the Chemical Bond", Cornell University Press, 1960, p. 324.
[17] Scharnow, *Z. anorg. Chem.*, 1933, **215**, 184; Scholder, *Angew. Chem.*, 1958, **70**, 583.
[18] Geilmann and Bode, *Z. analyt. Chem.*, 1950, **130**, 323.

other metallic salts are extremely soluble. Silver per-rhenate, which has been used to determine the atomic weight of rhenium, is only slightly soluble compared with the perchlorate. Salts of large organic bases (nitron, brucine, strychnine) are insoluble enough for the analysis of rhenium. The tetraphenyl-arsonium or -phosphonium salts are very much less soluble in water than in chloroform, and microanalysis of rhenium can be effected by solvent extraction of these salts.[19]

Reduction of Per-rhenates.—The per-rhenate ion resembles the perchlorate rather than the permanganate ion in its action towards reducing agents. The reduction of per-rhenates is usually slow and the mean state reached at a particular time must depend on the kinetics of the intermediate states through which they pass. An integral reduced state can be reached by adding an excess of reducing agent, preferably in a medium which can form a complex with the rhenium. In general, the higher the acidity, the higher the valency of the reduced state. Nitric and perchloric acids cannot be used as reducing media because reduced rhenium species catalyse their decomposition. The results of some investigations are summarised in Table 1.

TABLE 1.   *Chemical reduction of the per-rhenate ion*

Medium(N)	Reducing agent		Reduced state	Ref.
HCl(1—4)	Sn^{2+}, Ti^{3+}, V^{2+}, Cr^{2+}		4	20
H_2SO_4(1)	Sn^{2+}, Ti^{3+}, V^{2+}, Cr^{2+}		4	,,
H_2SO_4(18)	Cr^{2+}		5 + 4	,,
			(6 transient)	
	Sn^{2+}		5→4 + 7 slowly	,,
HCl(8—10)		Cr^{2+}	3	,,
		$2I^-$	5	,,
		$3I^-$	4	,,
H_2SO_4(<3·6)			0 + 1	21
H_2SO_4(10—18)	Zn—Hg		4	,,
HCl(0·6—3·2)			2 + 3	,,
HCl(4·8—6·4)			3 + 4	,,
H_2SO_4(9)	Cd—Hg		4	,,
,, (10—18)	Bi—Hg		5	,,
HCl	N_2H_4		4	22
HCl	H_3PO_2		4	,,

These results can be applied preparatively (see p. 380) and analytically. Thus per-rhenates, after reduction with bismuth amalgam, can be estimated volumetrically by re-oxidation to per-rhenate.[23]

[19] Ref. 2, p. 124.
[20] Tribalat, *Ann. Chim.*, 1949, **4**, 289.
[21] Lazarev, *Zhur. neorg. Khim.*, 1956, **1**, 385.
[22] Rulfs and Meyer, *J. Amer. Chem. Soc.*, 1955, **77**, 4505.
[23] Spitzy, Magee, and Wilson, *Mikrochim. Acta*, 1957, 354.

The polarographic reduction of per-rhenate is summarised in Table 2. The valency state reached is calculated from the Ilkovič equation.[24] The polarographic waves are irreversible and the half-wave potentials have no thermodynamic significance. The assignment of a three-electron reduction in perchloric acid has been questioned[25] because this value has only been obtained at one temperature. Gas is generated at the mercury surface, indicating decomposition of the acid as in chemical reductions.

TABLE 2. *Polarographic reduction of the per-rhenate ion*

Supporting electrolyte(M)	KCl(2)	HClO$_4$(4)	HCl(4)	KOH(0·1)	KCN(0·1)
Reduced state	−1	4	4	−1	5 and 1

The reduction to an apparent −1 state is discussed later.

Rhenium Trioxide.—The trioxide is a red paramagnetic solid which disproportionates *in vacuo* above 300° to the di- and the hepta-oxide. It is formed by allowing the heptaoxide to react with rhenium or the dioxide at about 300°. The trioxide is prepared more conveniently by decomposing the compound obtained from the heptaoxide and dioxan at 145°, or by heating the heptaoxide in carbon monoxide. It is remarkably inert to dilute acids and bases, provided that they are non-oxidising, so that rhenates (ReO_4^{2-}) must be prepared indirectly by fusing mixtures of rhenium dioxide and per-rhenate.

Rhenium Dioxide.—The dioxide is also paramagnetic. This black oxide can be obtained by partial reduction of ammonium per-rhenate, or rhenium heptaoxide, with hydrogen at 300°, or with rhenium at 600°. The hydrated oxide formed in hydrolysis of hexahalogenorhenates(IV) can be dehydrated *in vacuo* at 650°. It is soluble in acids, with which it forms complexes, but insoluble in bases. Aqueous oxidising agents convert it into per-rhenate. The rhenites containing the anions ReO_3^{2-}, ReO_4^{4-}, and ReO_5^{6-} are formed from the dioxide and fused alkalis.[26]

The compositions of the other oxides reported are rather uncertain. Thus the solid isolated by alkaline hydrolysis of rhenium trichloride was believed to have been a hydrated sesquioxide Re_2O_3. Similar hydrates of ReO and Re_2O, from per-rhenic acid reduced in hydrochloric acid with cadmium and zinc respectively, were also ill-defined.

The Halogen Compounds of Rhenium

This section of rhenium chemistry has been drastically revised in recent years. New compounds have been isolated and old ones contradicted.

[24] Colten, Dalziel, Griffith, and Wilkinson, *J.*, 1960, 71.
[25] Rulfs and Elving, *J. Amer. Chem. Soc.*, 1951, **73**, 3284.
[26] Deschanvres, *Ann. Chim.*, 1959, **4**, 1217.

The fluorine compounds are summarised in Table 3.

TABLE 3.   *Fluorine compounds of rhenium*

Oxidation state	Simple fluorides	Oxyfluorides	Complex anions
7	ReF_7[27]	$ReOF_5$ and ReO_2F_3[29] ReO_3F[32]	—
6	ReF_6[28]	$ReOF_4$[30] ReO_2F_2(?)[28]	ReF_8^{2-}(?) [33] $ReO_2F_4^-$ [34]
5	ReF_5[30]	—	ReF_6^- [35]
4	ReF_4[30]	—	ReF_6^{2-} [35a]

Simple Fluorides.—The heptafluoride has only recently been made[27] by passing fluorine at 250 mm. pressure over rhenium heated to 300—400°. The volatile product was purified by heating it at 400° in a static atmosphere of fluorine. The purity of the product is best judged from vapour-pressure measurements and as little as 0·1 % of rhenium hexafluoride can be detected in this way. Earlier workers believed that the hexafluoride was the highest fluoride attainable, and it is important to bear in mind that, in all previous work with the hexafluoride, contamination with the heptafluoride had been neglected.

The hexafluoride was originally made from fluorine and rhenium at 125°. Chlorine trifluoride has also been employed as a fluorinating agent. The hexafluoride should be heated with excess of rhenium metal to ensure the removal of any heptafluoride. According to Ruff and Kwasnik[28] it attacks silica at room temperatures. Later workers maintain that it is stable and only disproportionates above 300°. The hexafluoride can be reduced to the pentafluoride by tungsten carbonyl and an excess of tungsten hexafluoride. The pentafluoride disproportionates *in vacuo* above 180° to the tetra- and hexa-fluorides.[30] Ruff and Kwasnik made a tetrafluoride by reducing the hexafluoride with either hydrogen at 200° or sulphur trioxide at 400°, but it is believed to have been a mixture of tetra- and penta-fluorides.[30] Attempts to prepare lower fluorides from the trihalides and anhydrous hydrogen fluoride have been unsuccessful.[31]

Oxyfluorides.—Ruff and Kwasnik isolated $ReOF_4$ and ReO_2F_2 when a fluorine–oxygen mixture was passed over rhenium at 125—300°.

[27] Malm, Selig, and Fried, *J. Amer. Chem. Soc.*, 1960, **82**, 1510.
[28] Ruff and Kwasnik, *Z. anorg. Chem.*, 1932, **209**, 113; 1934, **219**, 65; Cady and Hargreaves, *J.*, 1961, 1563; Nikolaev and Ippolitov, *Doklady Akad. Nauk, S.S.S.R.*, 1960, **134**, 358.
[29] Aynsley, Peacock, and Robinson, *J.*, 1950, 1622; Cady and Hargreaves, *J.*, 1961, 1568.
[30] Hargreaves and Peacock, *J.*, 1960, 1099.
[31] Eméleus and Gutmann, *J.*, 1950, 2115; Peacock, *J.*, 1956, 167.
[32] (*a*) Engelbrecht and Grosse, *J. Amer. Chem. Soc.*, 1954, **76**, 2042; (*b*) Aynsley and Hair, *J.*, 1958, 3747; (*c*) Wiechert, *Z. anorg. Chem.*, 1950, **261**, 310.
[33] Hargreaves and Peacock, *J.*, 1957, 4390.
[34] Peacock, *J.*, 1955, 602.
[35] Peacock, *J.*, 1957, 467.
[35a] Weise, *Z. anorg. Chem.*, 1956, **283**, 377; Peacock, *J.*, 1956, 1291.

Robinson and his co-workers[29] disputed this and isolated only $ReOF_5$ and ReO_2F_3 If any sexivalent rhenium were present it would have given hydrated rhenium dioxide on hydrolysis by disproportionation, but only per-rhenic and hydrofluoric acids were found. Another septivalent oxyfluoride, ReO_3F, has been prepared from the corresponding chloride with hydrogen fluoride.[32a] or from potassium per-rhenate with iodine pentafluoride[32b] or anhydrous hydrogen fluoride.[32c] It is much more stable than permanganyl fluoride. The sexivalent $ReOF_4$ results when rhenium hexafluoride is reduced with rhenium carbonyl.[30] It closely resembles the analogous molybdenum and tungsten compounds.

Complex Fluorides.—Neither the hepta- nor the hexa-fluoride combines with alkali fluorides in the absence of a solvent. The hexafluoride, dissolved in iodine pentafluoride or liquid sulphur dioxide, does react and an impure salt K_2ReF_8 has been obtained.[33] Pure salts with rhenium in the sexivalent state which contained the $ReO_2F_4^-$ anion were readily prepared by dissolving per-rhenates in bromine trifluoride at room temperature.[34] No doubt more oxygen could be displaced under more extreme conditions. In the corresponding reaction with permanganates the manganese is reduced to the quadrivalent state (MnF_5^-). A series of salts of the ReF_6^- ion have been made by Peacock[35] who ingeniously adapted Ruff's original observation that rhenium hexafluoride oxidised potassium iodide, by using sulphur dioxide as a solvent, e.g. $2ReF_6 + 2KI = I_2 + 2KReF_6\downarrow$.

The hexafluororhenates(IV) are described later together with the other hexahalogenorhenates.

The remaining halogen compounds isolated are summarised in Table 4.

TABLE 4.   *Halogen compounds of rhenium*

Oxidation state	Simple halides	Oxyhalides	Complex anions
7		ReO_3Cl^{39} ReO_3Br^{37}	
6		$ReOCl_4$ $ReO_2Br_2^{40}$	
5	$ReCl_5^{36}$		$ReOCl_5^{2-}$ $ReOBr_5^{2-41}$
4	$ReBr_4^{37}$ ReI_4^{38}		$ReCl_6^{2-}$ $ReBr_6^{2-}$ ReI_6^{2-} $Re(OH)Cl_5^{2-}$ $Re_2OCl_{10}^{4-41}$
3	$ReCl_3$ $ReBr_3$ ReI_3^{38}		$ReCl_4^-$ $ReCl_6^{3-}$
1	ReI^{38}		

The highest authenticated chloride is the pentachloride, made by direct chlorination of the metal at 400—500° or by the action of carbon tetra-

[36] Knox, *J. Amer. Chem. Soc.*, 1957, **79**, 3358.
[37] Colton and Wilkinson, *Chem. and Ind.*, 1959, 1314.
[38] Peacock, Welch, and Wilson, *J.*, 1958, 2901.
[39] Wulf and Clifford, *J. Amer. Chem. Soc.*, 1957, **79**, 4257.
[40] Brukl and Ziegler, *Monatsh.*, 1933, **63**, 329.
[41] Trzebiatowski and Wajda, *Bull. Acad. Polon. Sci. Class III*, 1954, **2**, 249; Jezowski and Iodka, *Rocznicki Chem.*, 1939, **19**, 187.

chloride on rhenium heptaoxide at 400°.[36] It can be purified by sublimation *in vacuo* or in a current of chlorine. In water it disproportionates to hydrated rhenium dioxide and septivalent rhenium.

The existence of a tetrachloride has been disputed although the recent isolation of a tetra-bromide and -iodide indicates that the tetrachloride may exist. Croft[46] claims to have intercalated the tetrachloride in graphite. The trichloride resulted when the pentachloride was heated in an inert gas. It is also formed by thermal dissociation of silver hexachlororhenate(IV) or from sulphuryl chloride and rhenium. The original magnetic measurements showed the solid trichloride to be diamagnetic[42] and the molecular weight in acetic acid solution, corresponding to a dimer, accorded with this. However, a remeasurement has established the paramagnetism of the trichloride.[43]

Recently, complexes with organic ligands have been investigated.[44] Thus 1:1 and 1:2 complexes of rhenium trichloride and triphenylphosphine resulted when the acetone solutions of the components were mixed. More complicated products were obtained from nitrogen-containing ligands, with the exception of pyridine. For example, the complex with 1,10-phenanthroline was diamagnetic and was believed to be polymeric. Complexes with organic multiply-bonded compounds are also known.[37] Rhenium tribromide is probably very similar to the trichloride and has been prepared by analogous methods.

Rhenium iodides have only recently been isolated.[38,10] They cannot be made from the metal and iodine alone or in solvents, but only indirectly *via* complex iodides. Thus per-rhenic acid can be reduced with hydriodic acid to hexaiodorhenic(IV) acid which decomposes thermally to rhenium tetraiodide. The tetraiodide can be further decomposed; at 350°, in the presence of excess of iodine, to the tri-iodide; at 110°, if the iodine vapour is removed in a stream of nitrogen, to the monoiodide. All the halides can be decomposed to the metal at higher temperatures.

Oxyhalides are usually present in crude halides unless air and moisture are rigorously excluded during preparation. Per-rhenyl chloride can be made from rhenium chlorides and oxygen[39] or even from rhenium disulphide, chlorine, and oxygen. The corresponding oxybromide, prepared from the metal, melts at 39·5°.[40] Colton *et al.*, who passed oxygen over rhenium tetrabromide at 100—120°, obtained the oxybromide as a liquid at room temperatures.[44] On hydrolysis it yielded only bromide and per-rhenate. The original material was probably contaminated with the dioxydibromide.

Complex Salts.—The series $M_2[Re(halogen)_6]$, where M is an alkali, alkaline earth, or co-ordinated multivalent metal ion, is next in importance

[42] Schuth and Klemm, *Z. anorg. Chem.*, 1934, **220**, 193.
[43] Knox and Coffey, *J. Amer. Chem. Soc.*, 1959, **81**, 5.
[44] Colton, Levitus, and Wilkinson, *J.*, 1960, 4121.
[45] Meloche and Martin, *J. Amer. Chem. Soc.*, 1956, **78**, 5985.
[46] Croft, *Austral. J. Chem.*, 1956, **9**, 184.

to the per-rhenates as a starting point for other preparations. Apart from the fluoro-salt all can be made in the wet way by reducing acid solutions of per-rhenates with such agents as hypophosphorous acid,[22] chromous[44] and titanous chlorides,[20] and hydrazine.[20] Alkali iodides or bromides can also be employed as reductants, e.g.

$$2KReO_4 + 16HCl + 6KI = 2K_2ReCl_6 + 4KCl + 3I_2 + 8H_2O$$
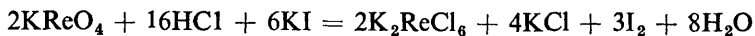
This overall equation hides the complexity of the reaction. The reduction goes through intermediate oxidation states because complex oxychlorides of quinquevalent rhenium can also be recovered from the eactiron mixture. The reaction can also involve a displacement of a hexaiodorhenate ion by hydrochloric acid. The equilibrium between the hexahalgenorhenates has not been measured, but qualitatively the constants pertaining to the displacement cannot be large, because it is possible to traverse the series

$$ReCl_6^{2-} \underset{HBr}{\overset{HCl}{\rightleftharpoons}} ReBr_6^{2-} \underset{HI}{\overset{HBr}{\rightleftharpoons}} ReI_6^{2-}$$
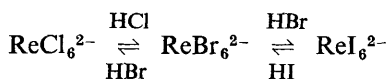
though with more ease to the right. In fact the most convenient preparation of the iodo-compound is by displacement of the chloro- or bromo-salt with hydriodic acid.[13] The salts can also be made in a dry way, for example by passing chlorine over a mixture of rhenium and potassium chloride.

Ruff and Kwasnik[28] claimed to have made the hexafluoro-salt using hydrofluoric acid with the potassium iodide and per-rhenate, but neither Peacock nor Weise[35a] could repeat this preparation and had to resort to dry methods. The former heated ammonium hexaiodorhenate(IV) with potassium bifluoride at 250°, the latter passed hydrogen fluoride over potassium hexabromorhenate at 450°. Other salts were made by precipitation or ion-exchange from the potassium salt.

The thermal and hydrolytic stabilities of the hexahalogeno-salts decrease from the fluoride to the iodide. The fluoride itself is stable in concentrated hydrochloric acid and can only be slowly attacked by aqueous alkali. For complete decomposition alkali fusion is required. The hexachlororhenates(III) are stable in 0·01N-hydrochloric acid, the hexabromo-compound in 2N-hydrobromic acid and the hexaiodo-compound only in concentrated hydriodic acid. Potassium chlororhenate(IV) can be distilled at 1100° whereas the iodorhenate starts to dissociate at 300°. The absorption spectra of the halogenorhenates have been utilised for rhenium analysis.

The salts $K_2[Re(OH)Cl_5]$, $K_2[ReOCl_5]$, and $K_4[Re_2OCl_{10}]$ were isolated from potassium per-rhenate, hydrochloric, and hydriodic acid mixtures by varying the iodide concentration and temperature.[46]

Lower Valency States Stabilised by Ligands

A series of stable compounds of all the lower valency states of rhenium has only just been completed, largely because of the interest shown in recent years in the ligand chemistry of transition metals in general.

The Cyanide Ligand.—The cyanide ion has been extensively applied as a ligand. Morgan and Davies[47] made $Na_3[Re^VO_2(CN)_4],2H_2O$ by reducing a mixture of sodium per-rhenate and cyanide with hydrazine. Recently the potassium salt has been studied in detail.[48] It was made from $K_2[Re^VOCl_5]$ with an alkaline solution of potassium cyanide. The presence of four ions in the complex oxy-cyanide was indicated by the conductivity of its dilute solutions, that of quinquevalent rhenium by oxidation with dichromate. Polarographic reduction gave a six-electron change in potassium chloride and a four-electron change in potassium cyanide to the same -1 and $+1$ states as were obtained from potassium per-rhenate (p. 376). Chemical reduction with sodium amalgam led to the $+1$ state. A complex of this state, $K_5[Re(CN)_6],3H_2O$ was prepared similarly by reducing a mixture of potassium hexachlororhenate(IV) with potassium amalgam,[49] and may have resulted from the sodium amalgam reduction of rhenium trichloride in sodium cyanide solution.[50] Other examples of this state with rhenium in the cation are the salts of the $[Re(CH_3 \cdot C_6H_4 \cdot NC)_6]^+$ ion.[51]

A complex cyanide of quinquevalent rhenium $K_3Re(CN)_8,H_2O$ was prepared from potassium hexaiodorhenate(IV) and potassium cyanide in methanol.[52] The similarity of its infrared spectrum to those of the octa-cyano-molybdenum and -tungsten complexes suggested the same dodecahedral co-ordination. A solution of the salt could be oxidised in acid solution by air, and the hexammine-cobaltic salt isolated from the solution:

$$4[Re^V(CN)_8]^{3-} + O_2 + 4H^+ = 4[Re^{VI}(CN)_8]^{2-} + 2H_2O.$$
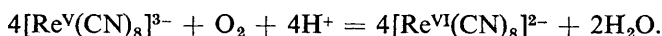
Alternatively it could be reduced to a tervalent complex ion $[Re^{III}(CN)_6]^{3-}$ with potassium borohydride.

Arsine and Phosphine Ligands.—The ligand o-phenylenebisdimethylarsine (L) stabilises the $2+$, $3+$, and $5+$ states of rhenium.

The compounds $[Re^{III}L_2(halogen)_2]^+ClO_4^-$ were prepared by reducing per-rhenic acid with hypophosphorous acid in the presence of the diarsine and appropriate halogen in methanol. Further reduction with sodium stannite produced the uncharged complexes, $[Re^{II}L_2(halogen)_2]^0$; oxidation with chlorine yielded the quinquevalent complex $[Re^VL_2Cl_4]^+$ ClO_4^-.[53] All these formulae were justified by analytical and magnetic evidence. Similarly, the $2+$ and the $3+$ state can be stabilised with triphenyl-phosphine.[54]

Rhenium Carbonyls and Carbonyl Halides.—These can be regarded as stable compounds of zero- and uni-valent rhenium with direct rhenium—

[47] Morgan and Davies, *J.*, 1938, 1858.
[48] Trzebiatowski and Danowska, *Z. phys. Chem.*, 1959, **212**, 29.
[49] Clauss and Lissner, *Z. anorg. Chem.*, 1958, **297**, 300.
[50] Meier and Treadwell, *Helv. Chim. Acta*, 1958, **38**, 1679.
[51] Malatesta, *Angew. Chem.*, 1960, **72**, 323.
[52] Colton, Peacock, and Wilkinson, *J.*, 1960, 1374.
[53] Curtis, Fergusson, and Nyholm, *Chem. and Ind.*, 1958, 625.
[54] Freni and Valenti, *J. Inorg. Nuclear Chem.*, 1961, **16**, 240.

carbon bonding. Druce's claim to have prepared such a bond in a trialkyl from rhenium trichloride and a Grignard reagent has been twice disproved.[2]

Rhenium pentacarbonyl can be made by the action of carbon monoxide on a variety of compounds (the trioxide, heptaoxide, heptasulphide or potassium per-rhenate) at about 200—300 atmospheres at 250°. It is stable to dilute acids and alkalis. Cryoscopic measurements, as well as its diamagnetism, shows that it is dimeric. Two series of carbonyl halides, $Re(CO)_5X$ and $[Re(CO)_4X]_2$[55] exist. The iodide of the first series was made by the reaction

$$2K_2ReI_6 + 10CO = 2Re(CO)_5I + 3I_2 + 4KI$$

and the others by the general reaction

$$Re + CuX + 6CO = Re(CO)_5X + Cu(CO)X$$
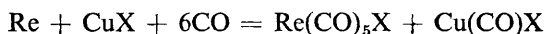
All are colourless solids which sublime without decomposition in an atmosphere of carbon monoxide. They are soluble in hydrocarbons but not in water. The second series was formed by heating members of the first series in inert solvents:

$$2Re(CO)_5X \rightarrow [Re(CO)_4X]_2 + 2CO$$
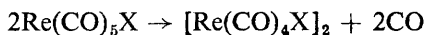
The tetracarbonyl halides cannot be melted without decomposition. A whole series of substitution reactions of the carbonyl halides has been adumbrated.[56] The carbonyls and carbonyl halides also react with hot methanolic potash to form the salt $K[Re_2(CO)_8O_2H]$[57].

Cyclopentadienyl Compounds.—When cyclopentadienylsodium interacted with rhenium pentachloride in tetrahydrofuran a yellow compound was isolated which as far as elementary analysis could show was the expected rhenocene $Re(C_5H_5)_2$, a member of the metallocene series, which ranges from titanium to nickel. However, a substance of this formula should be paramagnetic, whereas it was in fact diamagnetic. The problem was resolved by nuclear magnetic resonance spectroscopy[58] of solutions in organic solvents which showed two peaks whose areas were in the ratio of 10:1. The first peak was the expected one, corresponding to the ten ring protons, the second, which had a large chemical shift, was due to a diamagnetically shielded proton directly bound to rhenium. Similar transition metal–hydride links have been found subsequently.[59] The compound was therefore a univalent rhenium hydride. The hydride

[55] Abel, Hargreaves and Wilkinson, *J.*, 1958, 3149.
[56] Hieber and Fuchs, *Z. anorg. Chem.*, 1941, **248**, 269; Hieber and Schuster, *ibid.*, 1956, **287**, 214.
[57] Hieber and Schuster, *Z. anorg. Chem.*, 1956, **285**, 265.
[58] Green, Pratt and Wilkinson, *J.*, 1958, 3916, 4315.
[59] Lewis, *Sci. Progress*, 1961, **49**, 67.

behaved as a proton acceptor, or base, with a dissociation constant in dioxan very close to that of ammonia in the same solvent:

$$(C_5H_5)_2ReH \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} (C_5H_5)_2ReH_2^+$$
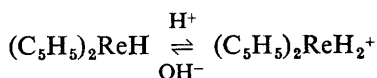
Salts of the cyclopentadienyl cation can be precipitated by large anions. A similar but non-hydridic cation with benzene ligands[60] $Re(C_6H_6)_2^+$ can also be isolated in salts. Doubtless the metallo-organic chemistry of rhenium will expand in line with work on other elements.

The Re^{-1} State

The existence of a rhenide ion analogous to halide ions seemed definite, if somewhat unexpected, until as recently as last year. However, nuclear magnetic resonance[60a] and infrared spectroscopy of rhenide solutions revealed the presence of metal–hydrogen bonds. The existence of a negative valency state became questionable because the reducing properties of solutions could be accounted for by the presence of hydrides. For simplicity, however, the reduced state is referred to as a rhenide.

Lundell and Knowles[11] first prepared a dilute solution of potassium rhenide by passing a cold solution of potassium per-rhenate in sulphuric acid through a column of amalgamated zinc. The colourless solution which emerged could be re-oxidised to per-rhenate in accordance with

$$Re^{-1} + 8Fe^{3+} = 8Fe^{2+} + Re^{7+}$$

The per-rhenates were also reduced to rhenide at the dropping mercury electrode (p. 376) but significantly the reduction goes further at very low concentrations.[24]

A solid rhenide approximating to KRe, $4H_2O$ has been made by reducing potassium per-rhenate with potassium in wet ethylenediamine.[61] Repeated extraction with isopropyl alcohol removed potassium hydroxide. The solid was slightly paramagnetic. A square planar structure which utilised dsp^2 orbitals for binding the water molecules to a rhenide ion was suggested and justified by Cobble on thermodynamic grounds. He considered, but rejected, the possibility of a rhenium hydride.[62]

Other workers used lithium reduction in aqueous solution and separated the lithium hydroxide by recrystallisation from water or isopropyl alcohol. The bulk of lithium hydroxide could be precipitated as phosphate. The lithium salt in solution could be converted into the ammonium salt on cation exchange resins, and then into other salts with appropriate alkalis.[63]

[60] Fischer and Wirzmuller, *Chem. Ber.*, 1957, **90**, 1725.
[60a] Colten, Dalziel, Griffith, and Wilkinson, *Nature*, 1959, **183**, 1755.
[61] Bravo, Griswald, and Kleinberg, *J. Phys. Chem.*, 1954, **58**, 18.
[62] Cobble, *J. Phys. Chem.*, 1957, **61**, 727.
[63] Floss and Grosse, *J. Inorg. Nuclear Chem.*, 1959, **9**, 318; 1960, **16**, 36.

Ginsberg[64] argues from the first workers' results that their reduction product, which analysed to a valency state between -0.8 and -1.3, was contaminated with per-rhenate and rhenium oxides and hence the pure product would have had a state below -1. He repeated the reduction with amalgamated zinc and obtained a $+1 \pm 0.1$ state, but with sodium amalgam a -2 to -3.5 state. Potassium rhenide was then prepared more carefully to yield a white diamagnetic solid reputedly free from alkali and per-rhenate. The oxidation state determined with calcium hypochlorite in alkali was $-3.4(5)$. This solid was treated with excess of sulphuric acid and, from a potassium analysis, the acid consumed, the hydrogen evolved, and the rhenium formed, the following equation was deduced:

$$K_3ReH_7 + 3H^+ = 3K^+ + Re^0 + 5H_2$$
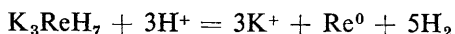
The empirical formula was doubled to avoid the paramagnetism which would arise from quadrivalent rhenium and, the water present being allowed for, the solid had the composition $K_6Re_2H_{14},6H_2O$. Nuclear magnetic resonance spectra again provided definite evidence of a rhenium hydride by the presence of a small peak to the high field side of the main water proton peak.[64] The ratios $H^-/H^+ = 2$ and $H^-/Re = 6.5$—7.3 were deduced, and agreed with the formula suggested by chemical analyses.[65]

Subsequent work has not lessened the confusion. Ginsberg now believes that the solid isolated from the reduction of potassium per-rhenate in wet ethylenediamine is anhydrous K_2ReH_8 with the rhenium in a -5 state. His earlier material appears to have been contaminated with carbonate and per-rhenate. Floss and Grosse however, having re-investigated their product, assign to it the formula $KReH_4$ with a variable amount of water of crystallisation.

Further work is obviously needed to see whether separate hydrides exist. Nevertheless, there is now little doubt that the existence of a simple rhenide ion analogous to halide ions is untenable.

Rhenium Compounds with Metallic Bonding

Rhenium forms compounds with metals and some non-metals in which the bonding is different from that considered previously. In particular this hexagonally close-packed metal tends to form intermetallic phases of wide ranges of composition and more complex structures with transition elements of Groups IV, V, and VI,[66] *e.g.* $ReZr_2$, Re_3Cr_2, $ReMo_2$ with the same structure as β-uranium, or $Re_{25}Zr_5$ and $R_{22}Nb$ with the α-manganese structure. Silicides,[67] borides,[68] a germanide,[69] and a nitride[70] are known,

[64] Ginsberg, Ph.D. Thesis, Columbia University, 1959, and private communication.
[65] Ginsberg, Miller, Cavanaugh, and Dailey, *Nature*, 1960, **185**, 528.
[66] Ageev, *Doklady Akad. Nauk*, *S.S.S.R.*, 1959, **129**, 559.
[67] Searcy and McNees, *J. Amer. Chem. Soc.*, 1953, **75**, 1578; 1955, 77, 5290.
[68] Searcy and McNees, *J. Amer. Chem. Soc.*, 1954, **76**, 5287; Aronsson, Stenberg, and Åselius, *Acta Chem. Scand.*, 1960, **14**, 733, 1001.
[69] Neshpor, Paderno, and Samsonov, *Doklady Akad. Nauk*, *S.S.S.R.*, 1958, **118**, 515.
[70] Hahn and Konrad, *Z. anorg. Chem.*, 1951, **264**, 174.

but contrary to earlier work[71] a carbide could not be detected.[13] Direct rhenium bonding also occurs in rhenium dioxide and rhenium carbonyl.

Comparative Chemistry of Rhenium

Stable compounds containing rhenium in the valency states from zero to seven have now been isolated. However, some of these states are only accessible because of ligand stabilisation, and the more normal chemistry of the oxygen and halogen compounds of rhenium shows the comparative instability of the uni-, bi-, and quinque-valent states. The last tends to disproportionate to the more stable quadri- and septi-valent states in aqueous media, and sometimes in the solid. This disproportionation of a quinquevalent state has analogies in the preceding group of the Periodic Table (e.g. S_2F_{10}, UCl_5).

Comparison with the Neighbouring Elements.—The significant difference between rhenium and manganese is the great stability of the latter's bi-valent state even in salts of oxy-acids. The usual argument forwarded for the stability of the Mn^{2+} ion is that it corresponds to a stable half-filled electronic level, $3d^5$, yet the $5d^5$ configuration of Re^{2+} is unstable. The counter argument that the stability of a half-filled level decreases as the atom becomes larger does not appear cogent when the ability of elements on either side of gadolinium to attain the half-filled gadolinium level $4f^7$, is considered, although the tendency is becoming apparent in the actinide series.

Ahrens[72] believes that bivalent manganese is the more stable because the gap between the third and the second ionisation potential of manganese is greater than the difference between the rhenium potentials, i.e. it is easier to oxidise bivalent rhenium. However, his thesis, even if true, does not account for the stability of bivalent manganese. It leaves us to explain the differences in ionisation potentials and furthermore, any conclusions would only apply to ions in the gas phase. Considering the transition metals as a whole, we can see the tendency for the higher valency states to be more stable both in the earlier members of the series, and the later members of the groups in the Periodic Table. Qualitatively this tendency can be associated with the bonding between the atomic nuclei and their valency electrons, and, quite simply, the stability of the higher valency states of rhenium compared with those of manganese results from the fact that the valency electrons of rhenium are farther from the nucleus and are less tightly bound.
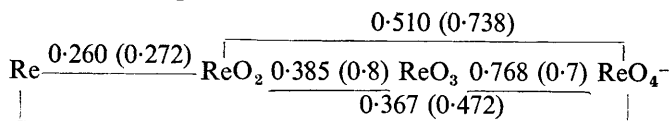
Even in the quadrivalent state, in which the two elements show the greatest resemblance, the tendency for Mn^{4+} to behave as an oxidising agent is very marked.

The differences between rhenium and technetium are of degree rather

[71] Trzebiatowski, Z. anorg. Chem., 1937, **233**, 376.
[72] Ahrens, J. Inorg. Nuclear Chem., 1957, **4**, 264.

than kind. It should be remembered that all the isotopes of the latter are radioactive and this very instability may influence chemical kinetics especially in solid-state reactions. Quantitatively the differences can be shown on a potential diagram,[73] which refers to acid solutions; the technetium potentials are in parentheses:

$$\text{Re} \underset{\underset{0\cdot367\ (0\cdot472)}{\underline{\hspace{5cm}}}}{\overset{0\cdot260\ (0\cdot272)}{\underline{\hspace{2cm}}}} \text{ReO}_2 \ 0\cdot385\ (0\cdot8)\ \overset{0\cdot510\ (0\cdot738)}{\overline{\text{ReO}_3\ 0\cdot768\ (0\cdot7)\ \text{ReO}_4^-}}$$

Thus both the sexi- and septi-valent state of technetium are more easily reduced to the quadrivalent state in acid solution. The difference in behaviour of per-rhenate and pertechnetate on polarographic reduction,[24] in which only a quadrivalent technetium state is reached in alkaline solution, could also be correlated with the potential diagram although the polarographic waves are irreversible.

When rhenium is compared with the Group VIII metals, a greater resemblance is seen between the chemistry of rhenium and ruthenium than that of the neighbouring osmium. Thus ruthenium forms a stable tribromide and trichloride but with osmium the tetrahalides are more stable; the dioxide of ruthenium is more stable than that of osmium, and the complex halides of ruthenium are reminiscent of the rhenium complexes, e.g. $RuCl_6^{3-}$, $RuCl_6^{2-}$, $[RuCl_5(OH)]^{2-}$, $(Ru_2OCl_{10})^{4-}$. Similarly one can present evidence for a greater resemblance between rhenium and uranium or molybdenum, than between rhenium and tungsten.

Thermochemistry.—The measured heats of formation and free energies are collected in Table 5. In the gaseous rhenium heptaoxide molecule, which is known to be monomeric, if tetrahedral rhenium co-ordination is

TABLE 5.   *Heats of formation and free energies of rhenium compounds*

Compound	$-\Delta H°_{298}$	$-\Delta G°_{298}$
	(kcal/mole)	
ReO_2	101	89
ReO_3 [74]	146	127
Re_2O_7 [74]	296	259
$HReO_4(aq)$ [74]	189	167
$KReO_4$ [74]	263	239
ReS_2 [75]	46	44
$ReCl_3$ [76]	63	48
$ReBr_3$ [76]	39	34
ReF_6 [28]	275	252
$ReSi_2$ [67]	—	55

[73] King and Cobble, *J. Amer. Chem. Soc.*, 1957, **79**, 1959; Cartledge and Smith, *J. Phys. Chem.*, 1955, **59**, 1111.
[74] Boyd, Cobble, and Smith, *J. Amer. Chem. Soc.*, 1953, **75**, 5783, 578.
[75] Juza and Biltz, *Z. Elecktrochem.*, 1931, **37**, 498.
[76] King and Cobble, *J. Amer. Chem. Soc.*, 1960, **82**, 2111.

assumed, there are eight rhenium–oxygen bonds and an average rhenium–oxygen bond energy of 139 kcal./mole [(heat of formation 296 + heat of sublimation 34 + heats of atomisation $2 \times 183 + 7 \times 59 \cdot 1$) $\div$ 8]. This can be compared with the rhenium–fluorine bond energy of 96 kcal./mole in rhenium hexafluoride.

We can compare the oxides by calculating the energy required to produce an atom of oxygen and leave rhenium in the metallic state. The values are close for the di- and tri-oxides (110 and 108 kcal./g-atom of oxygen, respectively) and are significantly greater than for the heptaoxide (101 kcal/g. atom).

Structural Chemistry.—This chemistry is based mainly on tetrahedral and octahedral co-ordination around rhenium. Rhenium trioxide has a structure consisting of octahedra of oxygen, with rhenium at the centre, linked at every corner.[77] This structure is closely related to the perovskite structures ($M^{II}Ti^{IV}O_3$) which have additional metal ions at the centre of the unit cells. Recently, similar phases $[Ba_2M^{II}]Re^{VI}O_6$ and $Ba[M^I_{0 \cdot 5}Re^{VII}_{0 \cdot 5}]O_3$, where M^I and M^{II} are uni- and bi-valent metals with interesting variations in their magnetic properties have been studied.[78] Rhenium dioxide is similarly built from oxygen octahedra, but in this structure they share two opposite sides and the remaining two corners to give a very distorted rutile (TiO_2) structure with alternately short and long Re–Re distances.[79] No single value for a Re^{IV} ionic radius can be given for such a structure. An orthorhombic modification is formed by annealing above 1050°.[80] Rhenium heptaoxide has an orthorhombic lattice ($a = 15 \cdot 25$, $b = 5 \cdot 48$, $c = 12 \cdot 5$ Å) with eight molecules in a unit cell[81] but the structure has still to be determined. The thermochemical data already mentioned indicate that the bonding is not the same as in the di- and tri-oxides and this is further indicated by its high solubility in water, as well as organic solvents, and its high vapour pressure. A molecular lattice, with tetrahedrally co-ordinated rhenium within the molecules, is probable. Tetrahedral co-ordination occurs in solid per-rhenates[82] and probably in the per-rhenate ion in solution because the Raman spectra of the isoelectronic triad OsO_4, ReO_4^-, and WO_4^{2-} are so similar.[83] Per-rhenyl chloride and fluoride are also tetrahedral.[42,84] There is an interesting shortening of the Re–O bond length in the latter which is well outside the error of microwave spectroscopic measurements, and again no single value can be assigned to a covalent tetrahedral radius of rhenium.

The rhenium–oxygen system is quite different from the molybdenum–

[77] Meisel, *Z. onorg. Chem.*, 1932, **207**, 121.
[78] Ward and Longo, *J. Amer. Chem. Soc.*, 1960, **82**, 5985; Sleight and Ward, *ibid.*, 1961, **83**, 1088.
[79] Magnéli and Andersson, *Acta Chem. Scand.*, 1955, **9**, 1378.
[80] Magnéli, *Acta Cryst.*, 1956, **9**, 1038.
[81] Wilhelmi, *Acta Chem. Scand.*, 1954, **8**, 693.
[82] Broch, *Z. phys. Chem.*, 1929, **136**, 22; Pitzer, *Z. Krist.*, 1935, **92**, 131.
[83] Woodward and Roberts, *Trans. Faraday Soc.*, 1956, **52**, 615.
[84] Lotspiel, *Diss. Abs.*, 1958, **19**, 340.

and tungsten–oxygen systems which contain a plethora of intermediate phases between their di- and tri-oxides. This is probably because of the volatility and stability of rhenium heptaoxide. Any intermediate oxide is able to disproportionate into the dioxide and heptaoxide. Deschanvres,[26] however, claims to have prepared a non-stoicheiometric dioxide rich in oxygen, by thermal decomposition of ammonium per-rhenate at 350— 450°, which can be converted into the orthorhombic dioxide by annealing at 600°. The excess of oxygen is removed as heptaoxide.

TABLE 6.   *Bond lengths and co-ordination in rhenium compounds*

Bond		Ref.	Rhenium co-ordina-tion	Bond length (Å)	Ionic radii
	ReO_2	79, 80	6	—	—
Re–O in	ReO_3	77	6	1·87	Re^{VI} 0·55
	ReO_4^-	82	4	—	—
Re–O in	ReO_3Cl	39	4	1·76	
Re–O in	ReO_3F	84	4	1·66	
Re–F in	ReF_6	86	6	1·93*	
	ReF_6^{2-}	35a	6	2·02	Re^{IV} 0·66
Re–Cl in	ReO_3Cl	39	4	2·23	
Re–F	ReO_3F	84	4	1·86	
	$ReCl_6^{2-}$	85a	6	2·37	Re^{IV} 0·56
Re–Br	$ReBr_6^{2-}$	85b	6	2·50	Re^{IV} 0·55
	metal	16	12	1·37	
$\frac{1}{2}$ (Re–Re)	$Re_2(CO)_{10}$	87	6	1·51	

* Estimate only.

Octahedral co-ordination occurs in the hexahalogenorhenates(IV),[85,45] rhenium hexafluoride,[86] and in the carbonyl. In the last molecule there is a direct Re–Re bond, which is longer than in the metal itself, and the octahedra are inclined at 45°.[87]

The bond lengths found in various structures (Table 6) enable some radii for rhenium in different valency states to be deduced. By subtracting the covalent bond radii of fluorine, chlorine, and bromine from the bond lengths of the hexahalogenorhenates(IV) values of 1·36, 1·38, and 1·38 Å, respectively, are obtained for the covalent octahedral radius of rhenium. This is very close to the metallic radius for twelve-fold co-ordination (1·37 Å) but the agreement is not so convincing if one uses the experimentally determined fluorine radius (0·72 Å)[88] which reduces the first value to 1·30 Å.

The ionic radius obtained from the hexafluororhenate ion also differs

[85] (a) Aminoff, *Z. Krist.*, 1936, *A*, **94**, 246; (b) Templeton and Dauben, *J. Amer. Chem. Soc.*, 1951, **73**, 4492.
[86] Gaunt, *Trans. Faraday Soc.*, 1954, **50**, 209.
[87] Dahl, Ishishi, and Rundle, *J. Chem. Phys.*, 1957, **26**, 1750.
[88] Ref. 16, p. 228.

from the values obtained from the chloride and bromide. The first value can be accepted as being more nearly an idealized Re^{IV} radius, and it does conform with the other radii including that of Re^V, which, because of the isomorphism between salts containing the SbF_6^- and ReF_6^- ions,[35] must be close to that of Sb^V (0·62 Å). Ahrens's attempt[89] to calculate ionic radii empirically from ionisation potentials, which yielded 0·56 and 0·72 Å for Re^{7+} and Re^{4+}, respectively, is evidently more optimistic than successful. His value for Re^{7+} is also unlikely because it is so close to the value at which tetrahedral co-ordination can change to octahedral (limiting radius ratio 0·414 Å).

Magnetochemistry.—The interpretation of magnetic data obtained from a variety of rhenium compounds affords a good test of modern theory[90] as well as distinguishing between alternative structures. In the rhenium atom the valency electrons are $5d^5 6s^2$, the d electrons having parallel spins and separately occupying orbitals of equal energy. When ligands are placed around the ionised rhenium atom the d orbitals are no longer of equal energy. For octahedral co-ordination three orbitals (d_ϵ) have lower energy than the remaining pair (d_γ), whereas for tetrahedral co-ordination the order is reversed. The energy difference is greater for octahedral than for tetrahedral co-ordination, and also for ions of the third transition series compared with the preceding series. The large energy separation tends to favour spin pairing, as against electron promotion to the higher level, in octahedral rhenium complexes with four to six d electrons. The stereochemical consequences expected from the pairing of these non-bonding d electrons are given in Table 7. The ideal moment is not achieved in all of these examples because of competing interactions such as spin-orbital coupling, antiferromagnetism, and temperature-independent paramagnetism. Magnetically concentrated solids are also exceptional.

It should be noted that in all the rhenium(v) complexes examined there are deviations from ideal behaviour. Spin orbital coupling could reduce the moments to about 1·2—1·5 but for very low values polymeric structures need to be postulated. The tetrahedral co-ordination for d_γ^4 has not been fully substantiated, but the measured diamagnetism is a strong indication of this geometry.

The diagnostic value of magnetic measurements is well illustrated by the diamagnetism of cyclopentadienylrhenium hydride which provided an essential clue to its structure.[58] Other examples are provided by the coupling of paramagnetic units to produce diamagnetic molecules, e.g. rhenium carbonyl[87] and complexes containing the Re^{IV}–O–Re^{IV} unit[41] complexed with halides or organic acids.

[89] Ahrens, *Geochim. Cosmochim. Acta*, 1952, **2**, 155.
[90] Gillespie and Nyholm, *Quart. Rev.*, 1957, **11**, 339; Figgis and Lewis in "Modern Coordination Chemistry," ed. by Lewis and Wilkins, London, Interscience, 1960.
[91] Colton, Levitus, and Wilkinson, *J.*, 1960, 5275.

TABLE 7. *Configuration and magnetic moment of some rhenium complexes*

Ref. to magnetism	Non-bonding electrons	Complex	Expected co-ordination	Moment Ideal (spin only)	Moment Obs.
52	d^1	$Re^{VI}(CN)_8$	Dodecahedral(?)	1·73	2·0
52	d^2	$Re^{V}(CN)_8^{3-}$	Dodecahedral*	0	0
48	d_ϵ^2	$Re^{V}OCl_5^{2-}$	Octahedral	2·83	0·48
48	,,	$Re^{V}O_2(CN)_4^{3-}$	,,	2·83	0
53	,,	$Re^{V}L_2Cl_2^+$	,,	2·83	~0·7
35	,,	$Re^{V}F_6^-$	,,	2·83	1·55
41	d_ϵ^3	$Re^{IV}(OH)Cl_5$	,,	2·83	2·9
35^a	,,	$Re^{IV}Cl_6^{2-}$	,, *	3·87	3·6
35^a	,,	$Re^{IV}Br_6^{2-}$	,, *	3·87	3·7
35^a	,,	$Re^{IV}F_6^{2-}$	,, *	3·87	3·3
52	d_ϵ^4	$Re^{III}(CN)_6^{3-}$	,,	2·83	2·6
53	,,	$Re^{II}L_2Cl_2^+$	,,	2·83	1·8—2·1
44	,,	$Re^{II}(Me \cdot CO \cdot CH = COMe)_3$	,,	2·83	2·3
44	$d_{yz}^2 d_{zz}^2$	$Re^{III}Cl_3, 2PPh_3$	Trigonal bipyramidal	0	0
91	d_γ^4	$Re^{III}Cl_4^-$	Tetrahedral	0	0
91	,,	$Re^{III}Cl_2, NMe_2 \cdot CS_2$	,, *	0	0
53	d_ϵ^5	$Re^{II}L_2Cl_2^0$	Octahedral	1·73	1·7—1·8
49	d_ϵ^6	$Re^{I}(CN)_6^{5-}$	,,	0	~0
51	,,	$Re^{I}(Me \cdot C_6H_4 \cdot NC)_6$	,,	0	0

$L = o\text{-}Me_2As \cdot C_6H_4 \cdot AsMe_2$

* Partial X-ray or spectral confirmation of structure available.

Applications

It might reasonably be asked why so much attention has been devoted to rhenium, the rarest of elements, over the last few years. First, rarity need not be equated with expense, and in fact rhenium is less expensive than some of the platinum and rare-earth metals because of its ready extraction from ores. Secondly, interest in high-temperature materials in diverse technical applications has prompted many investigations involving rhenium, and this in turn has tended to increase the supply and availability of the metal. The chemist is mainly interested in rhenium as another transition metal of variable valency whose properties and stabilities in different states have to be incorporated into present-day theory.

The metal and its compounds have found specialised outlets in the same way as the platinum metals. The metal itself is applied as a protective coating or as an inert foil or filament in closed systems, but as it is difficult to fabricate, workable alloys have been developed. These find advantageous application in thermocouple,[92] contact, and heating elements.

Chemically, rhenium and its compounds are most efficient catalysts[93] for hydrogenation, dehydrogenation, dehydration, isotopic exchange, and even oxidation reactions. Rhenium sulphides are especially useful for the first two. For example rhenium heptasulphide can selectively hydrogenate multiple-bond systems without hydrogenolysis of carbon–sulphur links in the same system.[94] The halides are potential but as yet unexploited catalysts. It is conceivable that in the future the reducing power of rhenium hydride compounds will provide a further contribution to the inorganic arsenal of the organic chemist.

[92] Hasse and Schneider, *Z. Phys.*, 1956, **144**, 256.
[93] Tropsch and Kassler, *Ber.*, 1930, **63**, 2149; Platonov, *Zhur. obshchei Khim.*, 1941, **11**, 590.
[94] Broadbent, Slaugh, and Jarvis, *J. Amer. Chem. Soc.*, 1954, **76**, 1519.