141. *The Magnetic Properties of Rhenium Halides. Part I. Rhenium Tetra-, Penta-, and Hexa-chloride.*

By D. BROWN and R. COLTON.

The preparation and properties of rhenium tetrachloride, pentachloride, and hexachloride are described. The magnetic susceptibility of rhenium hexachloride shows Curie–Weiss dependence ($\theta = 30°$, $\mu_{\text{eff}} = 2{\cdot}07$ B.M.) whereas for the tetrachloride and pentachloride there is marked deviation below 220° and 100°K, respectively. An attempt is made to explain the discrepancies between the results of previously published magnetic studies of the pentachloride.

THE preparations of rhenium tetrachloride[1] and rhenium hexachloride[2] have been described briefly elsewhere and we now present further details of their chemical and magnetochemical behaviour. Rhenium pentachloride has been known for many years[3] and there exist in the literature discrepancies between the magnetic properties observed by different authors.[4,5] Using repeatedly resublimed rhenium pentachloride we have obtained results which are generally similar to those of Schüth and Klemm,[4] but our observed susceptibilities are consistently higher. *X*-Ray powder diffraction data indicate that the tetrachloride is non-crystalline and that the pentachloride is of low symmetry. Further work is in progress to elucidate the structure of the latter compound.

Rhenium tetrachloride is unstable in moist air, being readily hydrolysed to the dioxide. It is appreciably soluble in acetone and in dry methyl cyanide, slightly soluble in diethyl ether, chloroform, and methyl acetate, but is insoluble in benzene and carbon tetrachloride. All the solutions are reddish-brown.

Magnetic Data.—Rhenium tetrachloride obeys the Curie–Weiss law over the temperature range 300—220°K. Below 220°K the susceptibility increases more rapidly with temperature than would be expected for a Curie–Weiss plot. The five high-temperature points indicate a Weiss constant, θ, of 158° and a magnetic moment, μ_{eff}, of 1·55 B.M. The magnetic moment is lower than would be expected for either of the possible electron

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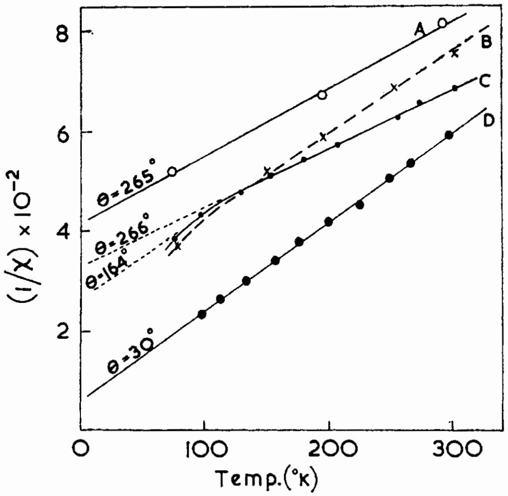
[1] Brown and Colton, *Nature*, 1963, **198**, 300.
[2] Colton, *Nature*, 1962, **194**, 374.
[3] Geilmann, Wrigge, and Biltz, *Z. anorg. Chem.*, 1933, **214**, 244.
[4] Schüth and Klemm, *Z. anorg. Chem.*, 1934, **220**, 193.
[5] Knox and Coffey, *J. Amer. Chem. Soc.*, 1959, **81**, 5.

configurations, and may be compared with the value of 0·9 B.M. recently obtained for rhenium tetraiodide,[6] suggesting that neither compound is magnetically dilute.

The magnetic susceptibility of rhenium pentachloride has been measured twice before [4,5] and, although both groups of workers agreed quite closely in their final values for the magnetic moment (2·3 and 2·21 B.M., respectively), there were large differences between their respective susceptibilities and θ values (Figure). Our results give $\theta = 266°$, almost identical with the value (265°) obtained by Schüth and Klemm,[4] and $\mu_{eff} = 2{\cdot}57$ B.M. On the other hand, Knox and Coffey [5] observed a deviation from the Curie–Weiss law below 150°K which was not reported by Schüth and Klemm who only measured susceptibilities at three temperatures. We have confirmed that there is indeed a deviation at approximately this temperature. The large difference between the θ value (164°) of Knox and Coffey and that obtained by us and by Schüth and Klemm may be due to the different preparative procedures employed. The usual method of preparation of the pentachloride, which was used by us and by Schüth and Klemm, is the chlorination of rhenium metal by use of chlorine gas, followed by sublimation of the product to remove traces of the more volatile hexachloride. Knox and Coffey,[5] however, prepared the pentachloride by the action of carbon tetrachloride on rhenium dioxide in a sealed tube. Small amounts of rhenium hexachloride, which was then unknown, may also be formed by this reaction. This would result in a marked lowering of the θ value and the slope of the plot of Knox and Coffey's results (Figure) suggests that this was in fact the case.



Plot of the reciprocal of the magnetic susceptibility against temperature, for rhenium penta- and hexa-chloride.

A, $ReCl_5$ (Schüth and Klemm [4]). B, $ReCl_5$ (Knox and Coffey [5]). C, $ReCl_5$ (this work). D, $ReCl_6$ (this work).

Rhenium hexachloride obeys the Curie–Weiss law very accurately between 98° and 300°K (Figure), giving $\theta = 30°$ and $\mu_{eff} = 2{\cdot}07$ B.M. which is high for a d^1 system. An independent measurement [7] gave a moment of 1·95 B.M. and, considering the method of filling the tube (see Experimental section), the agreement is satisfactory. Rhenium hexafluoride and technetium hexafluoride both have very low magnetic moments,[8] owing to spin–orbit coupling, and in the former instance it is known that the molecule is a perfect octahedron.[9] For rhenium hexachloride, spin–orbit coupling effects are not observed, presumably owing to some distortion from the perfect octahedral configuration. The magnetic properties of other rhenium(VI) chloro-compounds will be dealt with in further communications.

[6] Fergusson, Robinson, and Roper, *J.*, 1962, 2113.
[7] Clarke, private communication.
[8] Colton and Peacock, *Quart. Rev.*, 1962, **16**, 299, quoted as a personal communication.
[9] Woodward, personal communication.

The susceptibilities observed at various temperatures for the three compounds are shown in the Table.

Observed magnetic susceptibilities.

	Temp. (°K)	$\chi_m \times 10^6$ (c.g.s. units)		Temp. (°K)	$\chi_m \times 10^6$ (c.g.s. units)		Temp. (°K)	$\chi_m \times 10^6$ (c.g.s. units)
$ReCl_4$ ...	304	654	$ReCl_5$ ...	302	1457	$ReCl_6$ ...	297	1695
	275	695		274	1524		266	1872
	255	730		256	1591		251	1982
	240	766		207	1746		225	2201
	215	807		180	1840		201	2403
	189	888		154	1960		177	2672
	158	1016		123	2120		158	2942
	143	1132		99	2307		134	3358
	123	1311		77	2606		113	3876
	114	1418					98	4368
	96	1693						
	92	1840						
	87	2054						

EXPERIMENTAL

Preparation of Compounds.—(*a*) *Rhenium tetrachloride.* Pure rhenium dioxide, obtained by the water hydrolysis of rhenium pentachloride, was washed with water followed by acetone and vacuum dried. This material was refluxed with thionyl chloride for several hours and the insoluble black product, rhenium tetrachloride, was vacuum dried at room temperature after removal of the excess of thionyl chloride (Found: Re, 56·7; Cl, 43·3. Calc. for $ReCl_4$: Re, 56·8; Cl, 43·2%).

(*b*) *Rhenium pentachloride.* Commercial rhenium metal was heated at 700° in a stream of chlorine. At this temperature the amount of hexachloride obtained is very small. The product was distilled several times in the chlorine stream at a temperature as close as possible to its boiling point in order to prevent extensive decomposition to the less volatile trichloride. Traces of the hexachloride were readily removed during these sublimations owing to its being much more volatile than the pentachloride (Found: Re, 51·21; Cl, 48·69. Calc. for $ReCl_5$: Re, 51·26; Cl, 48·74%).

(*c*) *Rhenium hexachloride.* A concentrated solution of ammonium perrhenate was adsorbed on porous brick and dried at 100° in air. The small pieces of brick were loaded into a glass tube and the ammonium perrhenate was reduced with hydrogen, first at 250° to the dioxide, and then at 600° to the metal, formed as a reactive film dispersed throughout the brick. The hydrogen was displaced by oxygen-free nitrogen, and passage of chlorine over the metal at 600° gave an almost quantitative conversion into rhenium hexachloride which is extremely volatile and was readily separated from traces of the pentachloride by distillation in a stream of chlorine at 60° (Found: Re, 46·0; Cl, 53·4. Calc. for $ReCl_6$: Re, 46·6; Cl 53·4%). More details of preparation of the pentachloride and hexachloride from rhenium metal are already available.[3]

Magnetic Susceptibilities.—The three chlorides examined are all extremely reactive towards moisture and consequently measurements were made in sealed tubes. For the tetrachloride and pentachloride, the tubes were packed in a dry-box and then stoppered with small polythene bungs. However, this method was impracticable in the case of rhenium hexachloride because of its low melting point, and it was necessary to attach the sample tube to an evacuated vessel containing the hexachloride. The thin-walled seal between the tube and evacuated vessel was broken and the sample was melted and run into the tube. Inevitably, some irregularities in packing were encountered on cooling but these were minimised by repeated melting and freezing of the sample. Sample length was used as a criterion of good packing, a variation of *ca.* 0·2 cm. in a total sample length of 12·5 cm. being observed. The measurements were made by the Gouy method over the temperature range 77—300°K. The electromagnet (Newport Instruments Ltd.) was built to the design of Bates and Lloyd Evans [10] and gave a field of 5900 oersteds over a 7 cm. pole-gap at 20 amp. Temperature variation was obtained by equilibrating the cooling effect of liquid nitrogen and the heating effect of a coil wound round a copper cryostat block. The temperature controller was built to the design of Roberts,[11] the platinum control

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[10] Bates and Lloyd Evans, *Proc. Phys. Soc.*, 1933, *A*, **45**, 925.

[11] Roberts, *Elect. Eng.*, 1957, **23**, 57.

wire also being wound on the cryostat block. At temperature equilibrium, heating is intermittent, but the sample hanging in the block is held at a steady temperature owing to the large heat capacity of the copper. The actual temperatures were measured using a calibrated chrome–alumel thermocouple. Full details of the apparatus have been published elsewhere.[12]

Analysis.—Rhenium was determined colorimetrically using furil α-dioxime.[13] Chloride was determined gravimetrically as silver chloride after hydrolysis of the penta- and hexachlorides with dilute potassium hydroxide. However, this procedure gave irreproducible results for the tetrachloride and it was necessary to fuse this compound with a sodium hydroxide–sodium peroxide mixture as the first stage of analysis.

X-*Ray Data.*—*X*-Ray powder diffraction patterns were obtained with a 19 cm. Debye–Scherrer camera and a Guinier camera, using filtered Cu K_α radiation.

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CHEMISTRY DIVISION, ATOMIC ENERGY RESEARCH ESTABLISHMENT,
HARWELL, DIDCOT, BERKS.

[Present address (R. C.): DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF MELBOURNE,
PARKVILLE N.2, VICTORIA, AUSTRALIA.]

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[12] Colton, Report AERE–R 4186, 1963.

[13] Meloche, Martin, and Webb, *Analyt. Chem.*, 1957, **29**, 527.