[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

Magnetochemistry of Technetium and Rhenium[1]

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A magnetic susceptibility apparatus was constructed and the Faraday method was employed to make measurements on small quantities (20–200 mg.) of technetium and rhenium substances from 78 to 410°K. The heptavalent compounds showed a small, temperature independent paramagnetism, while the susceptibilities exhibited by the quadrivalent complex compounds followed the Curie-Weiss equation and gave effective magnetic moments which indicate three unpaired electrons. The susceptibilities of the dioxides, however, were small compared with manganese dioxide, and the Curie–Weiss relation was not obeyed. The magnetic behavior of metallic technetium and rhenium was found to be similar to that for manganese. A qualitative discussion of the susceptibilities shown by these three elements was made in terms of Pauling's theory of metals.

Previous investigations of the chemistry of the synthetic element, technetium, have been limited necessarily to methods requiring either tracer[3,4] or fractional milligram quantities.[5,6,7] Conventional chemical studies[8,9] have been made possible recently by the availability of gram amounts of this element. Knowledge of the magnetic susceptibilities of technetium compounds should be helpful in establishing the valence states of technetium, and might shed light on the bond types involved. The magnetic properties of numerous manganese compounds have been investigated extensively, while, on the other hand, rhenium compounds have received relatively little attention. Accordingly, in this work analogous compounds of technetium and rhenium were prepared, and their susceptibilities determined so as to make possible comparisons between them and their manganese congeners.

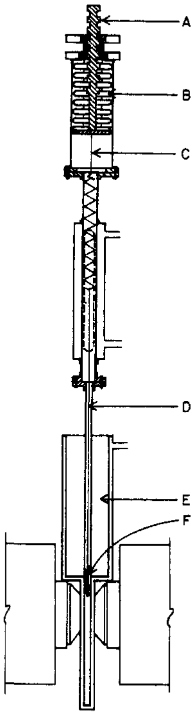

Fig. 1.—Magnetic susceptibility apparatus.

Experimental

Magnetic Measurements.—The susceptibility apparatus consisted essentially of an electromagnet to produce various field strengths with high field gradients and a spring to measure the forces experienced by samples placed in these magnetic fields. The electromagnet and power supply were procured commercially.[10] The forces were measured with a spring made of a special isoelastic spring alloy.[11] The spring (Fig. 1) was suspended from a Sylphon bellows, B, so that the entire internal assembly supporting the sample could be moved vertically by means of an external screw, A. Different lengths of quartz rod, C, were used between the spring and the bellows to place samples of varying weight in a definite position in the field. A long quartz fiber, D, with hooks at both ends was attached to the lower end of the spring, and the material the magnetic susceptibility of which was to be measured was contained in a small quartz bulb, F, suspended from the lower hook of the fiber.

The Faraday method for measuring magnetic susceptibilities was employed, since only fractional gram quantities of technetium were available. In this method a small sample in a magnetic field, H, experiences a force, $f = m\chi H\,dH/dz$, where m is the mass of the sample and dH/dz is the field gradient in a plane perpendicular to the pole faces. The spring was calibrated at room temperatures by adding known weights and noting the extensions produced. The sensitivity was 10.9 mg./mm. at the extensions employed. The product, $H\,dH/dz = K$, was determined as a function of the current in amperes flowing through the coils of the electromagnet by measuring the forces exerted on standard samples of known weights and susceptibilities. The values in Table I are the averages of measurements on ten different samples, including duplicates, which agreed usually to within 2–3%. Various concentrations of aqueous nickel chloride solutions, solid sodium chloride and pure water were used in the calibration. Values of the gram susceptibility, χ, for these standards were taken from Selwood[12] and from Ishiwara.[13] The field strength at the position selected for maximum force was determined by measuring the force on platinum wires of about 4 cm. length. When the wire is sufficiently long that one end experiences a negligibly small force compared with the other end, the force is given by, $f = {}^1/_2 \mathrm{K} H^2 A$, where K is the volume susceptibility and A is the cross-sectional area of the wire.

TABLE I

CALIBRATION OF MAGNETIC SUSCEPTIBILITY APPARATUS

Current, amp.	Field strength, oersteds	$K \times 10^{-7}$ oersted^2 cm.$^{-1}$	Current, amp.	Field strength, oersteds	$K \times 10^{-7}$ oersted^2 cm.$^{-1}$
1	2100	0.14	6	9100	2.75
2	4080	.54	7	9650	3.10
3	5860	1.11	8	10100	3.43
4	7380	1.78	9	10500	3.73
5	8420	2.33	10	10850	4.02

A variety of fluids was used in the chamber, E (Fig. 1), of an all-metal Dewar to maintain the various temperatures desired. The lowest temperatures were established by liquid nitrogen (78°K.) and by solid carbon dioxide mixed with trichloroethylene (197°K.). A temperature of 255°K. was obtained by circulating ethyl alcohol, cooled by an electric refrigerating unit containing a sodium chloride–water eutectic mixture, through the Dewar chamber. Temperatures of 300, 350 and 400°K. were obtained by circulating

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[2] This paper is based on a thesis by Cecil M. Nelson presented to the Department of Chemistry of the University of Tennessee in partial fulfillment of requirements for the Ph.D. degree, June, 1952.

[3] C. Perrier and E. Segre, *J. Chem. Phys.*, **5**, 712 (1937); *ibid.*, **7**, 155 (1939).

[4] J. F. Flagg and W. E. Bleidner, *ibid.*, **13**, 269 (1945).

[5] E. E. Motta, G. E. Boyd and Q. V. Larson, *Phys. Rev.*, **77**, 1270 (1947).

[6] S. Fried, THIS JOURNAL, **70**, 442 (1948).

[7] C. L. Rulfs and W. W. Meinke, *ibid.*, **74**, 235 (1952).

[8] G. E. Boyd, J. W. Cobble, C. M. Nelson and W. T. Smith, Jr., *ibid.*, **74**, 556 (1952).

[9] J. W. Cobble, C. M. Nelson, G. W. Parker, Wm. T. Smith, Jr., and G. E. Boyd, *ibid.*, **74**, 1852 (1952).

[10] Consolidated Engineering Corp., Pasadena, Cal. (Magnet, Model 3-104A; Power Supply, Model 3-121A.)

[11] John Chatillon and Sons, New York, N. Y.

[12] P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, pp. 28–29.

[13] T. Ishiwara, *Science Repts. Tohoku Imp. Univ.*, **9**, 233 (1920).

either water or silicone oil[14] from thermostat baths controlled by mercury regulators.

Dewar chamber temperatures were estimated using a copper–constantan thermocouple, and a differential thermocouple was employed to determine the departure of the temperature at the sample position from that of the chamber. Corrections for this difference were negligible, except at the following temperatures: 78° (+0.5°), 355° (−1.8°) and 405°K. (−3.5°). Helium at about 200 microns pressure was used as a heat transfer medium between the Dewar chamber and the sample.

All measurements were conducted at three different field strengths ranging from 6000 to 12000 oersteds to exclude the possibility that ferromagnetic impurities may have been present in the samples examined. The susceptibility was found independent of the field strength for all the compounds reported. Further, readings were made at zero current in the electromagnet coil both before and after a series of measurements to insure that no serious zero-point drifts had occurred. Corrections to the observed spring extensions, measured to 0.01 mm. with a traveling microscope, were made for the susceptibility contribution from the quartz sample container. The reproducibility of the magnetic measurements was limited by the reproducibility of the magnetic field, and by the difficulty of reproducing the sample position and alignment. The precision, except with substances of low susceptibility, was about ±2%.

Preparation of Technetium Substances. Elemental Technetium and Technetium Heptoxide.—Technetium compounds were prepared by methods similar to those already published for the analogous rhenium substances. The preparation of elemental technetium by hydrogen reduction of ammonium pertechnetate at 400–600° has been reported.[9] The metal, which is silvery grey in appearance, is easily oxidized to Tc_2O_7 in pure, dry oxygen at 400–600°.[8] The properties of technetium heptoxide are like those of Re_2O_7. Both compounds are very hygroscopic and dissolve in water to give strong acids. Upon neutralization of an aqueous pertechnic acid solution with ammonia and evaporation to dryness, white crystals of ammonium pertechnetate appear. X-Ray diffraction patterns taken on technetium metal[9] and on ammonium pertechnetate[8] show them to be isomorphous with the corresponding rhenium substances. The heptoxides, however, do not appear to be isomorphous.[15]

Technetium Dioxide.—Quadrivalent technetium compounds may be prepared by the reduction of ammonium pertechnetate in aqueous solutions by a method analogous to that employed with rhenium.[16] About 250 mg. of NH_4TcO_4 was dissolved in 25 ml. of water, and, after warming, 0.6 g. of granulated zinc and 12 ml. of hydrochloric acid (sp. gr. 1.19) were added. The solution was kept warm until all the zinc dissolved and kept distinctly acidic by additional acid. Technetium dioxide initially formed as a colloidal suspension, which, upon the addition of ammonia in an amount sufficient to redissolve the zinc hydroxide, formed a flocculent, readily filterable, black precipitate. This precipitate, after filtration, was washed with a very dilute ammonia solution, dried in air and then in an evacuated desiccator containing P_2O_5. Approximately 140 mg. of dry dioxide, which showed a molecular weight of 159 ± 2 (corresponding to $TcO_2 \cdot 1.6H_2O$), was recovered. Molecular weight determinations were performed by adding measured excesses of standard ceric sulfate solution to 5-mg. aliquots of the dioxide preparation to oxidize the Tc(IV) to Tc(VIII), and then back-titrating potentiometrically with standard KI solution. Formation of a definite hydrate, $ReO_2 \cdot 2H_2O$, has been reported[16] when Re(VII) compounds are reduced with zinc in hydrochloric acid solutions. In our susceptibility calculations the formula $TcO_2 \cdot 2H_2O$ was used, as the value of χ from the magnetic measurements was small, and hence subject to larger experimental uncertainties than those connected with the molecular weight.

Lower Technetium Oxides.—The thermal stability of TcO_2 was investigated in attempts to prepare lower oxides of technetium. Manganese dioxide when heated is reported[17] to lose oxygen to give Mn_2O_3, Mn_3O_4 and MnO successively, while ReO_2 decomposes into Re_2O_7 and metallic rhenium at high temperatures.[18]

Twenty milligrams of technetium dioxide dihydrate contained in a platinum boat was heated in vacuum in a quartz tube. After three hours at 300° to effect dehydration, the temperature was increased in steps of 50° every 15 minutes. At 900° a black solid began to deposit on the cooler portions of the tube, and after about one hour at 1100° approximately 50% of the material in the platinum boat had sublimed and condensed on the walls of the tube to form a brittle, black film. X-Ray diffraction patterns were taken on the residue in the boat, and on the volatilized material, and these were compared with the pattern given by TcO_2 prepared by thermal decomposition of NH_4TcO_4. All three patterns were identical, suggesting that technetium dioxide will sublime, *in vacuo*, without decomposition at temperatures above 1000°.

Potassium Hexachlorotechnetate (IV).—The procedure to prepare K_2TcCl_6 was quite similar to that already described[19] for K_2ReCl_6. Ammonium pertechnetate (200 mg.) was mixed together with 0.6 g. of KI and 25 ml. of hydrochloric acid (sp. gr. 1.19) and heated at a temperature just below boiling for about 30 minutes, taking care to replace acid lost by evaporation. After evaporation to near-dryness most of the potassium chloride in the mixture was extracted by washing with a 65% methanol–water solution. The technetium containing precipitate was then transferred to a 600-ml. beaker and digested with 200 ml. of hydrochloric acid until the volume was reduced to about two ml. After cooling the residue in an ice-bath, the golden-colored potassium hexachlorotechnetate(IV) crystals were transferred to a fine sintered-glass filter, washed with 65% methanol–water, and then dried with ethyl alcohol, ether and air. A yield of 42 mg. was obtained. X-Ray diffraction patterns[20] taken on K_2TcCl_6 and on K_2ReCl_6 prepared in a similar fashion showed the compounds to be isomorphous. Calculations for these simple cubic unit cells gave a_0 = 9.89 Å. for K_2TcCl_6 and a_0 = 9.842 Å. for K_2ReCl_6 compared with a_0 = 9.861 Å. reported in the literature[21] for the latter compound.

Attempted Preparation of Technetium Chlorides.—A variety of unsuccessful efforts were made to prepare some of the technetium chlorides. A direct union of technetium metal with gaseous chlorine was attempted by heating the former in an atmosphere of chlorine (p = 70 cm.) at 600° for several days. Only a very slight indication of a reaction could be observed. Reports of the preparation of several rhenium chlorides[22] by thermal decomposition of Ag_2ReCl_6 suggested that Ag_2TcCl_6 might be used to prepare the technetium chlorides. However, during the preparation of the latter compound it was found that an aqueous solution of K_2TcCl_6 slowly hydrolyzed to give TcO_2 which precipitated from solution. In contrast to the hexachlororhenate(IV) ion, a relatively concentrated hydrochloric acid solution is needed to prevent the hydrolysis of the $TcCl_6^=$ ion.

Thermal decomposition of K_2TcCl_6 did not seem to produce any volatile technetium compounds even at 1100°. When the reaction vessel was opened, however, the odor of chlorine was evident and the presence of Tc metal in the residue was established by X-ray analysis. Under the same conditions it was found that K_2ReCl_6 will distil without decomposition.

An immediate reaction at 300° was observed between dry, gaseous chlorine at one atmosphere and TcO_2 prepared by reduction of ammonium pertechnetate with zinc. As soon as chlorine entered the reaction tube a dark blue product condensed on the walls outside the furnace. Subsequently, a light brown product distilled from the hot zone when the temperature was gradually raised to 900°. The blue reaction product was distilled at 80–90° into a sample

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[14] Type DC-550, Dow-Corning Corp., Midland, Mich.

[15] R. D. Ellison, quoted by J. W. Cobble, "Thermodynamics of Technetium and Its Compounds," Doctoral Dissertation, University of Tennessee, Knoxville, Tennessee (1952).

[16] H. V. A. Briscoe, P. L. Robinson and E. M. Stoddart, *J. Chem. Soc.*, 666 (1931).

[17] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford University Press, London, 1950, p. 1273.

[18] N. V. Sidgwick, *ibid.*, p. 1306.

[19] L. C. Hurd and V. A. Reinders, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 178.

[20] R. D. Ellison, private communication (1952). See Ph.D. thesis, C. M. Nelson, University of Tennessee, Knoxville, Tenn. (1952).

[21] B. Aminoff, *Z. Kryst.*, **A94**, 246 (1936).

[22] W. Geilman and W. Wrigge, *Z. anorg. allgem. Chem.*, **214**, 258 (1933).

bulb, and then, at 500°, the brown product was sublimed into another bulb. Finally, the chlorine pressure was reduced to about 40 cm. and both sample tubes were sealed. Both of these products were strongly paramagnetic. Unfortunately, the chemical analyses of the blue and brown technetium compounds were inconclusive due to their hydrolysis in aqueous solutions prior to technetium and chlorine determinations.

Both products reacted similarly in the following respects: When water was added to the sample a reaction was noted. A dark product appeared which dissolved when hydrogen peroxide was added. In an attempt to ensure complete oxidation to the septivalent state, ammonium hydroxide was added and the solution heated. The solution turned yellow and a light brown precipitate formed. This precipitate would not dissolve upon continued heating. However, when nitric acid was added, the precipitate dissolved and the solution became colorless. If ammonium hydroxide was added again, the brown precipitate reappeared.

Preparation of Rhenium Substances.—Rhenium dioxide dihydrate was prepared according to the directions of Briscoe and co-workers.[16] The method is essentially that already described for the preparation of hydrated technetium dioxide.

Silver hexachlororhenate(IV) was formed by adding silver nitrate to an aqueous solution of K_2ReCl_6. The silver complex precipitate was separated on a sintered-glass filter, washed with water and dried in air.

In addition, a number of rhenium compounds were obtained on loan through the courtesy of Professor A. D. Melaven of the Chemistry Department of the University of Tennessee. These were: rhenium metal, NH_4ReO_4, $KReO_4$, Re_2O_7, ReO_3, K_2ReCl_6, $K_2Re(SCN)_6$, $Ag_2Re(SCN)_6$ and $Tl_2Re(SCN)_6$.

Experimental Results and Discussion

Magnetic susceptibilities of the technetium and rhenium substances described above are summarized in Tables II, III and IV where χ is the gram susceptibility, and χ_A the atomic susceptibility of the element, χ_M the molar susceptibility, and χ'_M is the susceptibility per gram atomic weight of technetium or rhenium. The agreement of the experimentally measured susceptibilities with those reported in the literature appears to be within the experimental errors involved. Where there is disagreement, the previously published values have been subjected to appreciable corrections for ferromagnetic impurities, which was not the case for the preparations used in our studies. The χ'_M values listed in the tables have been corrected for the various diamagnetic components[23,24] of the com-

Table II

Magnetic Susceptibilities of the Septivalent States

Compound	T, °K.	Gram susceptibility $\chi \times 10^6$	Molar susceptibility $\chi_M \times 10^6$	Gram-atomic susceptibility $\chi'_M \times 10^6$	$\chi \times 10^6$ (lit.)[a]
NH_4TcO_4	402	Decomposition			
	298	0.05	9	76	
	78	.08	14	81	
NH_4ReO_4	402	− .13[b]	−35	38	
	298	− .12	−32	41	−0.14 (T independent)
	78	− .11	−29	44	
$KReO_4$	402	− .10	−29	46	
	298	− .09	−26	49	−0.135 (T independent)
	78	− .06	−17	58	
Tc_2O_7	349	− .16	−50	23	
	298	− .13	−40	28	
	78	− .07	−22	37	
Re_2O_7	402	− .03	−16	46	
	298	− .03	−16	46	−0.03 (T independent)
	78	− .02	−10	49	

[a] N. Perakis and L. Capatos, *J. phys. radium*, **6**, 462 (1935). [b] Negative sign signifies diamagnetism.

Table III

Magnetic Susceptibilities of the Quadrivalent Complex Compounds

Compound	T, °K.	Gram susceptibility $\chi \times 10^6$	Molar susceptibility $\chi_M \times 10^6$	Gram-atomic susceptibility $\chi'_M \times 10^6$	$\chi \times 10^6$ (lit.)[a]
K_2TcCl_6	398	11.6	4520	4690	
	348	13.1	5110	5280	
	296	14.5	5650	5820	
	256	16.7	6500	6670	
	197	20.0	7800	7970	
	78	34.5	13470	13640	
K_2ReCl_6	403	7.23	3450	3640	
	352	8.15	3890	4080	
	298	9.50	4530	4720	8.78 (293°K.)
	256	10.80	5150	5340	
	197	13.1	6250	6440	12.0 (195°K.)
	78	22.1	10540	10730	19.3 (90°K.)
$K_2Re(SCN)_6$	401	4.29	2630	2880	
	350	4.91	3010	3260	
	299	5.39	3300	3550	
	254	6.37	3910	4160	
	197	7.23	4440	4690	
	78	11.2	6860	7110	
Ag_2ReCl_6	402	5.19	3190	3390	
	350	5.91	3640	3840	
	299	6.66	4100	4300	7.2 (293°K.)
	255	7.54	4640	4840	
	197	8.85	5450	5650	9.5 (195°K.)
	78	14.3	8800	9000	14.2 (90°K.)
$Ag_2Re(SCN)_6$	401	3.8	2850	3090	
	350	4.2	3150	3390	
	299	4.6	3460	3700	
	255	5.1	3840	4080	
	197	5.9	4440	4680	
	78	8.3	6230	6470	
$Tl_2Re(SCN)_6$	402	3.51	3320	3370	
	348	4.04	3810	3840	
	298	4.75	4480	4510	
	255	5.38	5080	5370	
	197	6.84	6450	6740	
	78	13.6	12830	13120	

[a] W. Schuth and W. Klemm, *Z. anorg. allgem. Chem.*, **220**, 195 (1934).

Table IV

Curie–Weiss Constants for Quadrivalent Complex Compounds

Compound	Curie constant C_M	"Mol. field" constant, Δ, °K.	Effective magnetic moment, μ_B, Bohr magnetons
K_2TcCl_6	2.3	87	4.3
K_2ReCl_6	1.7	57	3.7
Ag_2ReCl_6	1.8	120	3.8
$K_2Re(SCN)_6$	1.6	149	3.6
$Ag_2Re(SCN)_6$	1.9	212	3.9
$Tl_2Re(SCN)_6$	1.6	41	3.6

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[23] V. C. G. Trew, *Trans. Faraday Soc.*, **37**, 476 (1941).

[24] W. Trzebiatowski and P. W. Selwood, This Journal, **72**, 4505 (1950).

pounds investigated (*i.e.*, K^+, Ag^+, Cl^-) as well as for the underlying diamagnetism of the technetium or rhenium atoms[25] in their different oxidation states. These values for technetium were interpolated using values reported for molybdenum and ruthenium.[25] Thus, $-\chi_M \times 10^6$ was 24 and 6 for Tc(IV) and Tc(VII), respectively. The homopolar values reported by Trew[23] were used for the ligands in the complex ions of the quadrivalent states of technetium and rhenium.

It is to be expected that compounds of the septivalent states of technetium and rhenium would be diamagnetic as there are then no electrons in orbitals outside the rare gas cores of these elements. However, all of the compounds of the type R_2O_7 or MRO_4 examined in this work showed (Table II) a slight, temperature independent paramagnetism. Solid potassium permanganate has been reported[26] to show a small, temperature independent paramagnetism with $\chi_M = 5.4 \times 10^{-6}$, and other substances such as vanadium pentoxide, molybdenum trioxide and potassium dichromate[27] also appear to exhibit this behavior. An explanation may possibly be found in Van Vleck's treatment of paramagnetism[28] according to which a small, temperature independent paramagnetism may arise from fluctuations in the orbital angular momentum when there is more than one center of force. For atoms this would be zero, but for molecules where there are adjacent fields this term can be appreciable and may overshadow the normal atomic diamagnetism.

The quadrivalent complex compounds of technetium and rhenium were found paramagnetic (Table III), and the temperature variations of their susceptibilities obeyed the Curie–Weiss equation. Numerical values for the constants in this equation

$$\chi_M = C_M/(T + \Delta)$$

where C_M is the Curie-Weiss constant, and Δ is the "molecular field" constant, are summarized in Table IV. Effective magnetic moments for technetium(IV) and rhenium(IV), μ_B, in Bohr magnetons, were estimated using the relation: $\mu_B = 2.83\sqrt{C_M}$. These latter quantities are seen to be in fair agreement with numerical values estimated from the "spin only" equation: $\mu_B = \sqrt{n(n+2)} = 3.88$, using $n = 3$ as the number of unpaired electrons. The value of μ_B for Tc(IV), however, is larger than 3.9, while that for Re(IV) is slightly smaller. In some cases, the constant, Δ, is large. Since this quantity is in part a measure of the effect of the intramolecular environment on the paramagnetic atom, the results for Re(IV) may indicate some interaction between the ligands and the central atom. Further, this interaction appears to be more important for Re than for Tc(IV).[29] It seems possible in the technetium complex compounds that the orbital angular momentum may be incompletely quenched. Further, a comparison of their magnet moments with that estimated for K_2MnCl_6[30] suggests that the value of 4.3 Bohr magnetons for Tc(IV) is not unreasonable.

TABLE V

MAGNETIC SUSCEPTIBILITIES OF THE QUADRIVALENT AND HEXAVALENT OXIDES

Compound	T, °K.	Gram susceptibility $\chi \times 10^6$	Molar susceptibility $\chi_M \times 10^6$	Gram-atomic susceptibility $\chi'_M \times 10^6$	$\chi \times 10^6$ (lit.)
$TcO_2 \cdot 2H_2O$	398	1.35	225	293	
	348	1.41	235	303	
	300	1.46	244	312	
	256	1.63	272	340	
	197	1.86	311	379	
	78	3.4	568	636	
$ReO_2 \cdot 2H_2O$	398	0.24	61	139	
	348	.27	68	146	
	295	.29	74	152	0.2 (ReO_2)[a]
	256	.31	79	157	
	197	.39	99	177	
	78	.74	188	266	
ReO_3	402	0.07	16	68	
	298	.07	16	68	0.15[a]
	78	.07	16	68	
$MnO_2 \cdot 0.48\ H_2O$	298				44[b]
	193				51
	88				68

[a] W. Schuth and W. Klemm, *Z. anorg. allgem. Chem.*, **220**, 193 (1934). [b] T. E. Moore, M. Ellis and P. W. Selwood, THIS JOURNAL, **72**, 865 (1950).

While the magnetic moments for the quadrivalent complex compounds are in general agreement with the expected theoretical values, the susceptibilities for the dioxides are very low (Table V) and do not obey the Curie–Weiss relation. These susceptibilities also differ greatly from those[31] reported recently for manganese dioxide, for which $\mu_B = 3.9$. This effect may be due to an exchange interaction which occurs in substances of high magnetic concentration. In addition, the intense electric fields produced by the oxide ions, which affect the energy levels of the paramagnetic ion, will lower the magnetic moment. Rhenium trioxide also shows only a very weak paramagnetism (Table V).

In the metallic state the atoms of technetium and rhenium are somewhat closer together and the coördination numbers are larger than in their compounds. A very high magnetic susceptibility might be expected, for there are five unpaired d-electrons in the ground states of each of these elements. However, the susceptibilities were found quite low (Table VI). A theory of the metallic state by Pauling[32,33,34,35] may be applied to the

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(25) W. Klemm, *Z. anorg. allgem. Chem.*, **246**, 361 (1941).

(26) A. Cotton and B. Tsai, *Compt. rend.*, **214**, 753 (1942).

(27) S. Berkman and H. Zocher, *Z. physik. Chem.*, **124**, 318 (1926).

(28) J. H. Van Vleck, *Phys. Rev.*, **31**, 587 (1928).

(29) X-Ray diffraction measurements on the complex technetium and rhenium compounds also suggest that Δ should differ. These complex compounds do not have similar structures, excepting K_2TcCl_6 and K_2ReCl_6 which are isomorphous. Consequently, it may be expected that the electric fields from the ions surrounding the paramagnetic atom may be different, and that this will be reflected to some degree by the "molecular field" constant.

(30) S. S. Bhatnagar, B. Prakash and J. C. Maheshwari, *Proc. Indian Acad. Sci.*, **10A**, 150 (1939), give $\chi_M = 6416 \times 10^{-6}$ at 27°. Assuming $\Delta = 70°$ a value, $\mu_B = 4.3$ may be obtained.

(31) T. E. Moore, M. Ellis and P. W. Selwood, THIS JOURNAL, **72**, 865 (1950).

(32) L. Pauling, *Phys. Rev.*, **54**, 899 (1938).

(33) L. Pauling, THIS JOURNAL, **69**, 542 (1947).

(34) L. Pauling, *Proc. Roy. Soc.* (*London*), **A196**, 343 (1948).

(35) L. Pauling, *Physica*, **15**, 23 (1949).

interpretation of the magnetic properties of manganese, technetium and rhenium. According to this theory, d-orbitals may be involved in bonding in the metallic state, and usually one or more orbitals, termed "metallic orbitals," are available for the unsynchronized resonance of the bonds. Manganese may be assumed on this view to possess valences of six and four. The electronic structure (A) of the first is presumed to consist of six electrons forming covalent bonds while one unpaired electron is placed in an atomic orbital. The other structure (B) then consists of four bonding electrons with three unpaired electrons in atomic orbitals. Both structures have two "metallic" orbitals.

Structure	d	s	p	Valence	Unpaired electrons
A	↑	.	. o o	6	1
B	↑ ↑ ↑ . .	.	. o o	4	3
C	. . . . .	.	. o o	7	0

The proper "valence" of technetium and rhenium metals may be derived from their structures and interatomic spacings. From a study of the variation of atomic radii with position in the Periodic Table, Pauling has derived a simple empirical relation between the radius for a given coördination number and the average valence. Using this relation, a valence of six is predicted for Tc and Re. The assignment of a higher valence to technetium and rhenium than to manganese seems to be consistent with the magnetic observations, for a higher valence implies fewer unpaired electrons, and hence a lower susceptibility (*cf.* Table VI). On the basis of the magnetic susceptibilities rhenium must have the highest valence. Further, from the susceptibilities it would appear that electron structure A is more important for Tc than for Mn. Another structure, C, may also contribute to a small extent to the resonating structures. Although C may be more important for rhenium than for either manganese or technetium, it seems likely that A is the predominant structure for all three metals.

TABLE VI

MAGNETIC SUSCEPTIBILITIES OF THE ELEMENTS

Element	T, °K.	Gram susceptibility $\chi \times 10^6$	Atomic susceptibility $\chi_A \times 10^6$
Mn	298	..	527^a
Tc	402	2.5	250
	298	2.7	270
	78	2.9	290
Re	402	0.37	69
	298	.37	69
	78	.35	66
	Independent of T		68.2^b

[a] M. A. Wheeler, *Phys. Rev.*, 41, 331 (1932). [b] N. Perakis and L. Capatos, *J. phys. radium*, 6, 462 (1935).

In some cases, as Pauling has pointed out, the valences assumed for the metallic state are the same as those for the compounds of the element. This similarity may be seen to exist in the cases of Mn, Tc and Re. Lower valences such as four and two are more stable in manganese compounds, while the valence of seven seems to be more stable in technetium and rhenium compounds. The melting points of the metals increase from manganese to rhenium. This indicates stronger binding which in terms of Pauling's theory, would mean a higher valence.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Isotopic Exchange Reactions of Neptunium Ions in Solution. I. The Np(V)–Np(VI) Exchange

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The isotopic exchange reaction between NpO_2^+ and NpO_2^{++} in 1 M $HClO_4$ at 0 and 10° has been measured. At 0° k = 29 mole^{-1} liter sec.$^{-1}$. The energy of activation, E_{exp}, has been found to be 8.3 kcal. and the entropy of activation, $\Delta S^{\pm}$, to be -24 cal. deg.$^{-1}$ mole^{-1}. This result is discussed in terms of an electron transfer mechanism for a homogeneous exchange reaction.

The isotopic exchange reactions between the various oxidation states that neptunium exhibits in perchloric acid solutions are of considerable interest. It is feasible to study the exchange between the two oxygenated species, NpO_2^+ and NpO_2^{++}, between an oxygenated ion, NpO_2^+, and a tetrapositive ion and between a tri- and a tetrapositive ion in such solutions. The analytical problem is simplified because of the two available isotopes of neptunium; Np^{237} is an α-emitter with a 2.20×10^6 year half-life while Np^{239} is a β-emitter with a 2.33 day half-life. Therefore the measurements of alpha to beta ratios furnish sufficient analytical data for determining the fraction exchanged. This communication represents the first of a series of such studies and concerns itself with the exchange between Np(V) and Np(VI) in perchloric acid.

Experimental

The Np^{239} was prepared by bombarding uranium in the Argonne National Laboratory pile and was purified by standard radiochemical methods.[1] The purity of the tracer was checked by following the decay of a suitably mounted aliquot. The tracer was found to be radiochemically pure. The Np^{237} solutions were spectroscopically pure.

The tracer was mixed with a solution of Np^{237}, and a Np(V) solution in 1 M perchloric acid was prepared by a pro-

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(1) P. Fields, Vol. 14B Div. IV NNES, "The Transuranium Elements," McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 1128.