May 26, 1952

To the Graduate Council:

I am submitting to you a dissertation written by James W. Cobble entitled "The Thermodynamics of Technetium and Its Compounds." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

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THE THERMODYNAMICS OF TECHNETIUM AND ITS COMPOUNDS

A DISSERTATION

Submitted to
The Graduate Council
of
The University of Tennessee
in
Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

---

by

James W. Cobble

June, 1952

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To

Margaret Ann

TABLE OF CONTENTS

CHAPTER		PAGE
I.	INTRODUCTION.	1
II.	PREPARATION AND IDENTIFICATION OF COMPOUNDS	4
	A. Preparation of Technetium Metal	4
	B. Preparation of Technetium Heptoxide.	7
	C. Preparation of Pertechnic Acid.	9
	D. Ammonium Pertechnetate.	9
	E. Preparation of Technetium Dioxide	12
	F. Technetium Trioxide	17
	G. Other Compounds of Technetium	19
III.	VAPOR PRESSURE STUDIES.	21
	A. The Vapor Pressure of Technetium Heptoxide.	21
	B. The Vapor Pressure of Pertechnic Acid	32
	C. The Vapor Pressure over Saturated Pertechnic Acid	35
IV.	CALORIMETRY	39
	A. The Heat of Combustion of Technetium Metal.	39
	B. The Heat of Solution of Technetium Heptoxide. . . .	53
	C. The Heat of Dilution of a Pertechnic Acid Solution.	56
V.	OXIDATION REDUCTION CELLS	61
	A. Acid Cell	62
	B. Basic Cell.	67

CHAPTER PAGE

VI. THERMOCHEMICAL CALCULATIONS 72

A. The Free Energies, Heats and Entropies of Formation of Technetium (VII) Compounds. . . 72

B. The Free Energy, Heat and Entropy of Formation of Technetium Dioxide 78

C. The Free Energy, Heat and Entropy of Formation of Technetium Trioxide. 79

D. The Oxidation-Reduction Scheme for Technetium 82

E. Comparison of the Properties of Sub-Group VII 82

VII. SUMMARY 94

APPENDIXES. 96

I. X-RAY DIFFRACTION POWDER PATTERNS 97

II. PHYSICAL CONSTANTS. 103

III. TREATMENT OF THE CALORIMETRIC DATA. 105

IV. THE HEATS OF COMBUSTION OF RHENIUM AND RHENIUM TRIOXIDE. 108

V. ESTIMATION OF ENTROPY VALUES FOR TECHNETIUM AND ITS COMPOUNDS. 115

BIBLIOGRAPHY 122

LIST OF TABLES

TABLE		PAGE
I.	Weight Loss Study on the Hydrogen Reduction of Ammonium Pertechnetate	6
II.	Analysis of Technetium Dioxides	15
III.	Summary of Known Technetium Compounds	20
IV.	The Vapor Pressure of Solid Technetium Heptoxide	27
V.	The Vapor Pressure of Liquid Technetium Heptoxide	28
VI.	Comparison of Thermodynamic Properties of Technetium and Rhenium Heptoxides	31
VII.	The Dissociation Pressure of Pertechnic Acid.	33
VIII.	The Vapor Pressure of Water over Saturated Pertechnic Acid Solutions	37
IX.	Thermodynamic Data for Solvation Reactions of Technetium and Rhenium Heptoxides	38
X.	Heat of Combustion of Paraffin Oil Accelerator.	46
XI.	Benzoic Acid Combustion Calibration	48
XII.	Heat of Combustion of Technetium Metal.	50
XIII.	Calibration of Solution Calorimeter	57
XIV.	Heat of Solution of Technetium Heptoxide.	58
XV.	EMF of the Technetium Dioxide-Pertechnetate Electrode in Pertechnic Acid Solutions.	65

TABLE PAGE

XVI. EMF of the Technetium Dioxide-Pertechnetate Electrode in Basic Solution 70

XVII. The Heat of Formation of Potassium Pertechnetate 77

XVIII. Summary of Thermodynamic Properties of Technetium and Its Compounds 83

XIX. Comparison of Properties of Sub-Group VII 87

XX. Comparison of X-ray Diffraction Patterns for Technetium and Rhenium Heptoxides 98

XXI. Comparison of Technetium Metal X-ray Patterns. 99

XXII. Interplanar Distances for Technetium Dioxide Prepared by Pyrolysis of Ammonium Pertechnetate 101

XXIII. Physical Constants. 104

XXIV. Heat of Combustion of Rhenium Metal 110

XXV. The Heat of Combustion of Rhenium Trioxide. 112

XXVI. Summary of Entropies Estimated for Technetium and Some of Its Compounds 121

LIST OF FIGURES

FIGURE PAGE

1. Potentiometric Titration of a 0.1 M. Pertechnic Acid Solution. 10
2. Beer's Law Plot for Aqueous Ammonium Pertechnetate Solutions 13
3. Sickle Gauge 22
4. Sickle Gauge (Photograph). 23
5. Vapor Pressure Apparatus 26
6. Vapor Pressure of Technetium Heptoxide 30
7. Vapor Pressure of H_2O over $HTcO_{4(s)}$ and $HTcO_{4(sat.)}$ . . 34
8. Combustion Calorimeter 40
9. Combustion Calorimeter 41
10. Micro-Combustion Bomb. 43
11. Solution Calorimeter 54
12. Oxidation-Reduction Diagram for Technetium 85
13. Oxidation-Reduction Diagram for Sub-Group VII. 91
14. X-ray Powder Pattern for Technetium Dioxide. 102
15. Time-Temperature Curve for Calorimeter 106

CHAPTER I

INTRODUCTION

The recent[1] large scale separation of technetium from the uranium fission products at the Oak Ridge National Laboratory has made possible an investigation of the chemistry of technetium using much larger quantities than have previously been available. Although element 43 was reported by the Noddacks in 1925[2], they have not published any further information on the element. In 1935[3] Perrier and Segrè bombarded molybdenum in a cyclotron with energetic deuteron particles and produced an isotope whose chemistry followed that expected for element 43. Because of the criticism of the Noddacks' evidence of element 43[4], and the further fruitless attempts of others to repeat their work[5,6], it now seems well established that the first bona fide chemical evidence for element 43 was that of Perrier and Segrè. The International Union of Chemistry has accepted their claim and the name which they gave to it, technetium.[7]

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(1) Performed by the "Hot" Laboratory Group, Chemistry Division, Oak Ridge National Laboratory.

(2) Noddack, W., Tacke, I., and Berg, O., Naturwissenschaften, 13, 567 (1925).

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

(4) Prandtl, W., Z. angew. Chem., 39, 1049 (1926).

(5) Prandtl, W., Ber., 60, 621 (1927).

(6) von Hevesy, G., Chem. Rev., 3, 321 (1927).

(7) Committee on New Elements, International Union of Chemistry, Chem. Eng. News, 27, 2996 (1939).

Until the occurrence of the chain reacting pile, only unweighable quantities had been produced by cyclotron bombardments of molybdenum; much of the previous "tracer" chemistry has been summarized recently by Hackney.[8] Since the War fractional milligram quantities[9] have been produced by prolonged neutron irradiation of molybdenum in the Oak Ridge National Laboratory graphite reactor. Milligram quantitites were also isolated[10] from fission product solutions from project sources in 1948. In the summer of 1951, fractional gram quantities became available for research purposes.[11]

It was felt that a thermodynamic study of the element and its compounds would be of primary interest in helping complete the thermodynamic data available on the transition elements. Such data are of aid in understanding the role of the d electrons in chemical bonding. In addition, the chemical similarities and differences of technetium and rhenium could best be demonstrated by quantitative data. Finally, such information should aid in predicting the stability of, as yet, unknown technetium compounds.

In this dissertation heats of solution, of oxidation and combustion, of vaporization and sublimation, and free energies of reaction for some of the well identified valence states of technetium are reported.

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(8) Hackney, J. C., J. Chem. Ed., 28, 186 (1951).

(9) Motta, E. E., Boyd, G. E., and Larson, Q. V., Mon-C-169 (1946); Phys. Rev., 72, 1270 (1947).

(10) Parker, G. W., Reed, J., and Ruch, J. W., AECD-2043 (1948).

(11) We are indebted to G. W. Parker and his group at the Oak Ridge National Laboratory for making available this element for the research presented in this dissertation.

By use of some semi-theoretical considerations of entropy, both free energies and enthalpies of technetium compounds have been calculated from the experimental data. The stability, the redox scheme, and some of the bond strengths of technetium and its compounds have been calculated and compared with the information available for other members of Group VII. In general, the thermodynamic behavior of technetium and its compounds has been found to be that predicted from the position of the element in the periodic table. A few noteworthy exceptions, however, have been found.

CHAPTER II

PREPARATION AND IDENTIFICATION OF COMPOUNDS

Since the previous work on technetium had been performed on quantities of a few milligrams or less, it was desirable to prepare larger amounts of the element and compounds, and to identify, characterize, and prove their formulas by analysis. Technetium metal provides the best starting material, and it will be described first.

A. Preparation of Technetium Metal

The technetium was obtained from the "Hot" laboratory at the Oak Ridge National Laboratory. It consisted of about 1 g. of technetium as tetraphenylarsonium pertechnetate with perchlorate carrier dissolved in 10 l. of concentrated sulfuric acid. In addition to the technetium , the crude material also contained considerable amounts of radioactive ruthenium, although it was not present in quantities large enough to be considered chemically as but a trace impurity . In addition, small quantities of rhenium were also present, since this material had been used by the "Hot" laboratory as a stand-in to test the separation procedure of technetium from the fission products.

It was found that the tetraphenylarsonium pertechnetate could be electrolytically decomposed by electrolysis of liter quantities of the concentrated sulfuric acid solution with large surface area platinum electrodes to give a solid product. Subsequent distillation of the solid formed from sulfuric, perchloric and nitric acid mixtures

gave a distillate from which technetium sulfide could be precipitated. The detailed procedure is described elsewhere,[1] but briefly it consisted of dissolving the sulfide in ammoniacal hydrogen peroxide to give ammonium pertechnetate and ammonium sulfate. This solid was then heated in a stream of hydrogen in a quartz tube. The reduction proceeded rapidly at low (200-300°) temperatures and the sample was finally raised to high enough temperatures (500-600°) to sublime the ammonium sulfate away from the technetium metal. The metal was demonstrated to have the same $\sin^2\theta$ and intensity values as the X-ray pattern taken by Mooney[2, 3] on metal prepared by sulfide reduction.[4] Further, the procedure could be used to reduce pure ammonium pertechnetate quantitatively to the metal as shown by data on reduction time as a function of loss in weight. (See Table I.)

Contrary to published results,[5] the metal would not dissolve in hydrochloric acid of any concentration, hot or cold, nor would it react with ammoniacal hydrogen peroxide as does metallic rhenium. It did dissolve, however, in aqua regia and dilute or concentrated nitric acid, in agreement with similar studies by Fried on smaller quantities.[6]

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(1) Cobble, J. W., Nelson, C. M., Parker, G. W., Smith, W. T., Jr., and Boyd, G. E., J. Am. Chem. Soc., 74, 1852 (1952).

(2) Mooney, Rose C. L., Acta Cryst., 1, 161 (1948).

(3) For this data, see Appendix, Part I.

(4) Fried, S., J. Am. Chem. Soc., 70, 442 (1948).

(5) Hackney, J. C., J. Chem. Ed., 28, 186 (1951).

(6) Fried, S., op. cit.

TABLE I

WEIGHT LOSS STUDY ON THE HYDROGEN REDUCTION OF AMMONIUM PERTECHNETATE

Wt. of Sample before Heating	Heating Time	Heating Temperature	Wt. after Heating	Formula for Residue
14.57 mg.	1 hr.	275°	8.23 mg.	78.1% TcO_2 or 103.3% Tc
8.23	1	350	8.02	100.6% Tc
8.02	1	400	7.97	100.0
7.97	1	500	7.97	100.0
7.97	1	900[a]	7.82	97.5
7.82	1	500	7.82	97.5

[a]Some loss of technetium metal by volatilization is indicated at this higher temperature.

The metal will also burn in oxygen to form technetium heptoxide,[7] but reaction with chlorine proceeds very slowly, if at all.[8]

The pure, freshly reduced metal is silvery-white, similar in appearance to rhenium prepared by ammonium perrhenate reduction. It tarnishes in moist air to give a grey powder. The density from X-ray data (assuming an atomic weight of 99.0) is 11.50 g./cc.[9], and the melting point is 2140°.[10] The ionization potential of the metallic gas is 7.45 volts.[11]

B. Preparation of Technetium Heptoxide

Technetium can be burned in dry oxygen at 400-500° to give technetium heptoxide, Tc_2O_7, in an analogous manner to that used to prepare rhenium heptoxide.[12] The yellow solid formed melts at 120°, is extremely hygroscopic, and dissolves in water to give a solution of pertechnic acid, $HTcO_4$. The details of the proof of the formula

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(7) Boyd, G. E., Cobble, J. W., Nelson, C. M., and Smith, W. T., Jr., J. Am. Chem. Soc., 74, 556 (1952).

(8) Nelson, C. M., "The Magnetochemistry of Technetium and Rhenium", Doctoral Dissertation, The University of Tennessee, 1952.

(9) Mooney, R. C. L., Acta, Cryst. 1, 161 (1948); Phys. Rev., 72, 1269 (1947).

(10) Parker, G. W., and Martin, W. J., Oak Ridge National Laboratory, Chemistry Division Quarterly Report for Period Ending December 31, 1951, ORNL-1260.

(11) Meggers, W. F., J. Research Natl. Bur. Standards, 47, 7 (1951).

(12) Melaven, A. D., Fowle, J. N., Brickell, W. and Hiskey, C. F., "Inorganic Synthesis", Vol. III, McGraw Hill, New York, N. Y., 1950, p. 188.

of this oxide have been previously described.[13] The oxide, as well as rhenium heptoxide, was tested for its electrical conductivity by distilling it into a small glass bulb which contained two tungsten electrodes and measuring the (D.C.) resistance. Rhenium heptoxide was found to conduct in the molten state, but technetium heptoxide apparently behaves quite differently. The solid at room temperature is non-conducting, but as the temperature is raised towards the melting point, the sample begins to show conductance which increases with increasing temperature until the melting point is reached. At its maximum conductance, it conducts about one-fourth as well as fused zinc chloride in the same apparatus. When the melting point is reached, however, the conductance rapidly drops to zero, and remains so up to the boiling point. This may apparently be some type of a premelting phenomenon; the melting point is rather low compared to rhenium heptoxide, although their boiling points are comparable. The melting process in technetium heptoxide is also accompanied by an abnormally large entropy change (See Chapter III). Technetium heptoxide is not isomorphous with rhenium heptoxide. (See Appendix I.)

Solutions of technetium heptoxide in concentrated sulfuric acid were observed to demonstrate various colors (red, green, blue) supposedly due to ions such as TcO_3^+ TcO_4^- similar to those postulated for manganese.[14]

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(13) Boyd, G. E., Cobble, J. W., Nelson, C. M., and Smith, W. T., Jr., J. Am. Chem. Soc., 74, 556 (1952).

(14) Latimer, W. M., and Hildebrand, J. H., "Reference Book of Inorganic Chemistry", McMillan Company, New York, N. Y., 1943, p. 374.

C. Preparation of Pertechnic Acid

It has been shown[15] that when an aqueous solution of technetium heptoxide is slowly evaporated over a solution of sulfuric acid at room temperature, crystals are formed which analyze as $Tc_2O_7 \cdot H_2O$ or $HTcO_4$. These crystals are reddish black in appearance[16] and are deliquescent. If the dehydration is continued for a long enough time, the compound will loose its water and form the heptoxide. The acid is even more unstable in this respect than perrhenic acid; the vapor pressure characterization of this compound will be discussed in Chapter III.

Aqueous solutions of pertechnic acid show all of the characteristics of "strong" acids. Figure 1 is the potentiometric titration curve for a 0.1 M. solution of pertechnic acid with 0.5 M. sodium hydroxide solution. From the inflection point at a pH of 6.5 ± 0.5, it may be concluded that the ionization constant of the acid is > 0.1.

D. Ammonium Pertechnetate

Ammonium pertechnetate remains from the evaporation of aqueous solutions of pertechnic acid to which an excess of ammonium hydroxide has been added. The crystal structure of the compound has been deter-

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(15) Boyd, G. E., Cobble, J. W., Nelson, C. M., and Smith, W. T., Jr., J. Am. Chem. Soc., 74, 556 (1952).

(16) Boyd, G. E., Cobble, J. W., Nelson, C. M., and Smith, W. T., Jr., loc. cit.

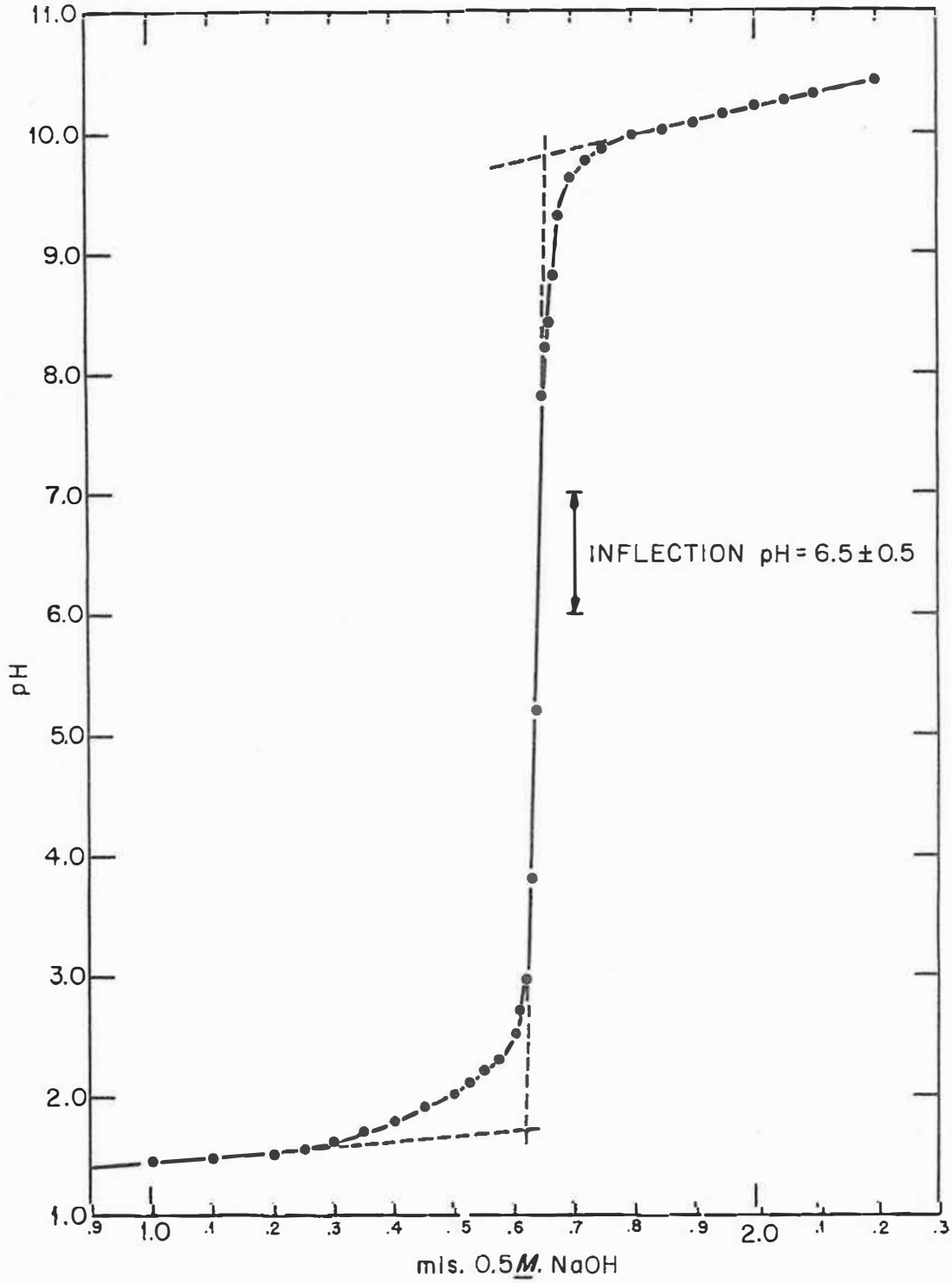


FIGURE I.- POTENTIOMETRIC TITRATION
OF A 0.1 M. PERTECHNIC ACID SOLUTION

mined:[17] it is tetragonal and the unit cell contains 4 molecules. It is also isomorphous with ammonium perrhenate and ammonium periodate. The lattice dimensions indicate that the perrhenate ion is larger than the pertechnetate ion. Its density is 2.73 g. cc.$^{-1}$.

The salt is white when pure, can be dried in an oven at 95 - 105°, is non-deliquescent, and has proved a convenient gravimetric form in analyzing pertechnic acid solutions and technetium heptoxide samples. Recently, however, Rulfs and Meinke[18] have questioned the stability of the salt under normal drying-oven conditions. Since their observations, based on half-milligram quantities, were contrary to our previous experience, it seemed desirable to check them with larger samples. A 100 mg. sample was heated in a covered platinum dish at 80-100° for eight days. After this time the sample had lost only 0.3 mg. or 0.3 percent, having lost 0.26 percent, which was probably water, in the first 24 hours. From these and many other observations, we conclude that the pure salt is relatively stable under these conditions. The same observations have been made by others on ammonium perrhenate.[19]

The pertechnetate ion has a strong ultraviolet absorption spectrum.[20] This spectrum, which contains two strong peaks at 2470 A.

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(17) Zachariasen, W. H., Argonne National Laboratory Report, ANL-4082, 1947; to be published in Acta. Cryst.

(18) Rulfs, C. L., and Meinke, W. W., J. Am. Chem. Soc., 74, 235 (1952).

(19) Smith, W. T., Jr., Private Communication, 1951.

(20) Boyd, G. E., Cobble, J. W., Nelson, C. M., and Smith, W. T., Jr., J. Am. Chem. Soc., 74, 556 (1952).

and 2890 A., can be used for the quantitative determination of pertechnetate ion solutions. A Beer's law plot determined with a Beckman Model DU Spectrophotometer and fused silica cuvettes is shown in Figure 2. Because of the high absorption, this method can be used to determine extremely small quantities of technetium.

E. Preparation of Technetium Dioxide

Fried[21] has reported that a black compound, isomorphous with rhenium dioxide, is formed when ammonium pertechnetate is heated at 400-500° according to the following reaction:

$$NH_4TcO_4 \xrightarrow{\Delta} \tfrac{1}{2}N_2 + 2H_2O + TcO_2 \qquad (II\text{-}1)$$

The reaction must be carried out in a sealed tube to prevent sublimation loss of the ammonium salt. Because Fried's samples were so small, it was not possible for him to carry out a chemical identification of the substance, and his evidence is based largely upon X-ray diffraction comparisons.

Accordingly, the preparation has been attempted using somewhat larger samples (5-10 mg.) and analyzing them by conventional semi-micro methods. The black residue left after pyrolysis in a sealed quartz tube was dissolved in an excess of standard ceric sulfate solution and then the excess ceric was back-titrated with standard iodide. The dissolving of the oxide was rather slow, requiring about one-half hour.

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(21) Fried, S., Private Communication to G. E. Boyd, 1950.

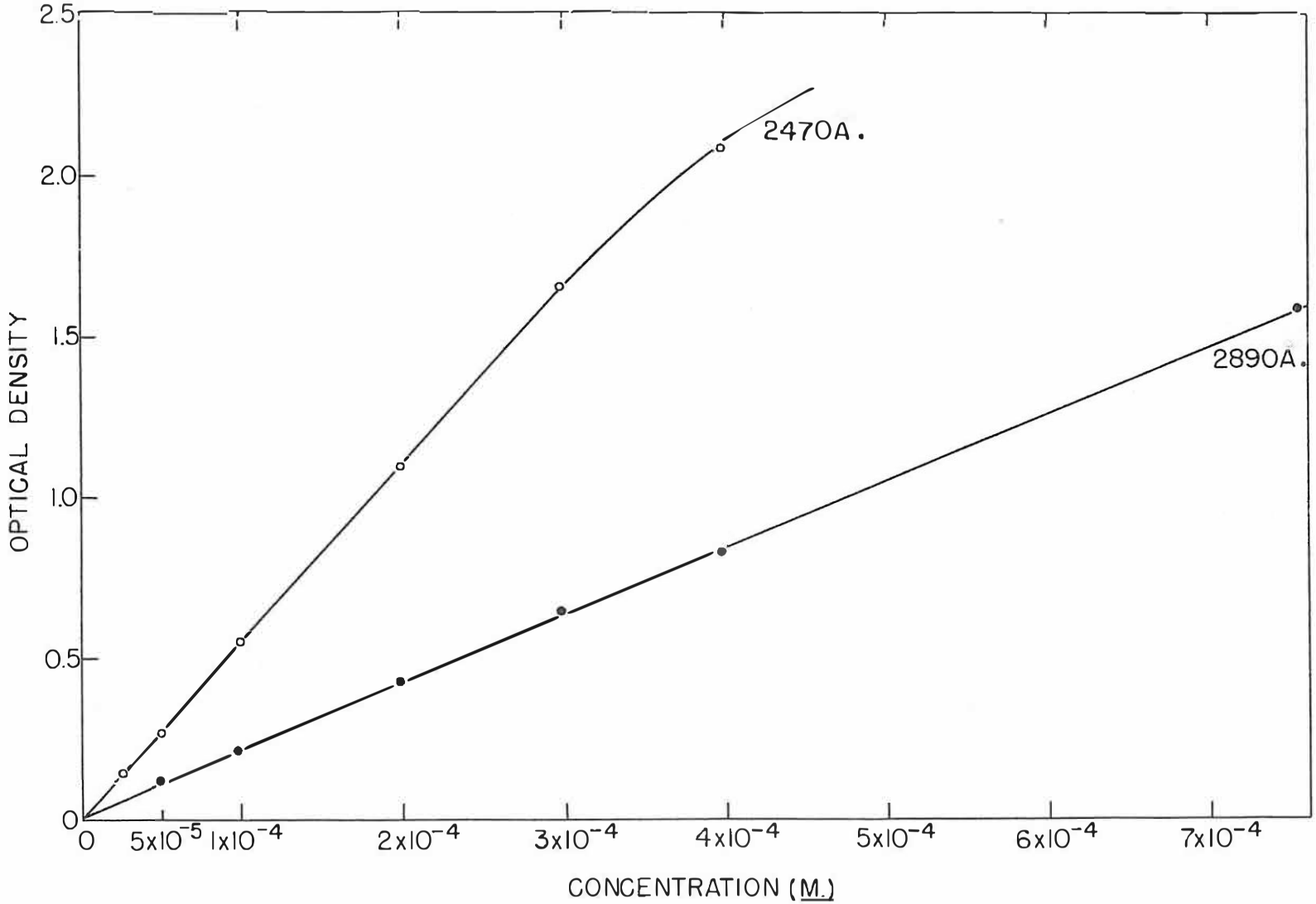


FIGURE 2.- BEER'S LAW PLOT FOR AQUEOUS AMMONIUM PERTECHNETATE SOLUTIONS

There is no apparent direct reaction between technetium dioxide prepared in this manner and dilute iodide solutions as is known in the case of manganese. Table II summarizes some analyses carried out on milligram amounts of the black compound prepared by pyrolysis. The molecular weight was calculated assuming that the oxidation by ceric ion is as follows:

$$TcO_2 + 2H_2O = TcO_4^- + 4H^+ + 3e^- \qquad (II\text{-}2)$$

This reaction has been found to hold for rhenium dioxide samples.[22] The X-ray diffraction pattern of sample I (see Table II) was also taken and was found not to be the same as that reported by Fried, nor is it the same as that found for TcO_2 hydrate prepared by solution reduction.[23] This might be explained in terms of various high temperature modifications of the compound, or by the fact that the products of the pyrolysis are not adequately stated by equation (II-1). It should be noted (see Table II) that the compounds formed have empirical formulas corresponding to either TcO_2 or TcO_2 hydrate. However, since they were all prepared under about the same conditions, there may be other oxides formed also. The apparent agreement, then, to compounds of TcO_2 or the hydrate may be fortuitous, although the X-ray diffraction pattern of TcO_2 prepared in this manner is the same as the TcO_2 prepared by heating TcO_2 hydrate in a vacuum at high

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(22) Geilman, W., and Wrigge, F. W., Z. anorg. u. allgem. Chem., 222, 56 (1935).

(23) Nelson, C. M., "The Magnetochemistry of Technetium and Rhenium", Doctoral Dissertation, The University of Tennessee, 1952.

TABLE II

ANALYSIS OF TECHNETIUM DIOXIDES

Run	Conditions	Sample Wt.	M.e. Wt.	Mol. Wt.[a]	Nearest Formula Wt.	Percent Nearest Formula Wt.
I	Sealed Tube 200-300° (2 hr.)	3.08 mg. 3.18	45.8 44.4	137 133	TcO_2 : 131	103
			Average	135		
II	Sealed Tube 200-300° (2 hr.)	1.73 4.86	58.9 57.6	177 173	$TcO_2 \cdot 2H_2O$: 167	105
			Average	175		
III	Evacuated Tube 200-300° (2 hr.)	3.20 3.55	55.2 50.0	166 177	$TcO_2 \cdot 2H_2O$: 167	103
			Average	172		
IV	Sealed Tube 600° (2 hr.)	3.12 3.35 4.40	52.6 60 45.9	158 180 138	$TcO_2 \cdot 2H_2O$: 167	95
			Average	159		

[a]Assuming 3 equivalents per mole of Tc(IV).

temperatures. (See Appendix I).

The black material so prepared can be titrated directly with ceric sulfate solution, although the titration proceeds very slowly. The reaction is:

$$3Ce^{+4} + TcO_2 + 2H_2O = TcO_4^- + 4H^+ + 3Ce^{3+} \qquad \text{(II-3)}$$

From the inflection voltage of this titration, however, the oxidation potential of equation (II-2) can be estimated from the formula:[24]

$$E_{infl.} = \frac{aE^o_{red.} + bE^o_{oxd.}}{a + b} \quad , \qquad \text{(II-4)}$$

where $E_{infl.}$ is the inflection voltage of the potentiometric titration, and a and b are the coefficients in equation (II-3) for the oxidizing agent (ceric) and reducing agent (TcO_2). $E^o_{red.-oxd.}$ stands for the standard potentials of the ceric-cerous and the technetium dioxide - pertechnetate systems. Using 1.44 volts for the cerous-ceric potential[25] and the observed inflection voltage of 940 ± 100 millivolts, we calculate the standard potential for the TcO_2-TcO_4^- electrode to be -0.6 volts. The limit of error in this estimate is about ± 0.2 volts (or larger). The largest uncertainty is the solubility of the technetium dioxide. It will be seen, however, that this voltage is in agreement with the standard potential of this electrode system as measured directly. (See

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(24) Kolthoff, I. M., and Furman, N. H., "Potentiometric Titrations", John Wiley and Sons, New York, N. Y., 1931, p. 45.

(25) Kolthoff, I. M., and Furman, N. H., op. cit., p. 280.

Chapter V).

TcO_2 hydrate has also been prepared by Nelson[26] from the solution reduction of pertechnetate solutions with zinc and hydrochloric acid. It has been characterized by him and was also used in this research. The X-ray diffraction pattern has also been taken for this compound, but it was similar neither to the pattern given by sample I (see Table II) prepared by pyrolysis in this research nor to that obtained by Fried.

It has been found that TcO_2 can be plated out on a platinum electrode (cathode) from neutral or basic solutions. While the black material so formed has not been identified chemically, it gives the same potential for the dioxide-pertechnetate electrode as the TcO_2 prepared by Nelson. We can conclude, then, that the material plated out must be pure TcO_2, or that any other products which may have been formed did not affect the voltage of the cell. The details of this cell identification appear in Chapter V.

F. Technetium Trioxide

During the preparation of technetium heptoxide a red material is frequently formed in the combustion tube which behaves somewhat differently than the red solutions of concentrated pertechnic acid. This later solution becomes colorless on dilution, while the red material formed above when dissolved in water to give a very dilute

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(26) Nelson, C. M., "The Magnetochemistry of Technetium and Rhenium", Doctoral Dissertation, The University of Tennessee, 1952.

colored solution (yellowish) apparently decomposes to give a black residue and pertechnetate ion. The black residue is technetium dioxide.

The same behavior has been noticed with the red material obtained when organic vapors are allowed to come in contact with technetium heptoxide. Since rhenium trioxide is red, it may be that the red material so obtained is technetium trioxide. If this is true, then this compound is more like the +6 valence state of manganese than of rhenium. The probable reaction between water and technetium trioxide can be written stepwise:

$$TcO_{3(s)} + H_2O_{(l)} + aq. = 2H^{+}_{(aq.)} + TcO_4^{=}{}_{(aq.)} \qquad (II\text{-}5)$$

$$3TcO_4^{=}{}_{(aq.)} + 4H^{+}_{(aq.)} = 2TcO_4^{-}{}_{(aq.)} + TcO_{2(s)} + 2H_2O_{(l)} \qquad (II\text{-}6)$$

Rhenium trioxide is insoluble in water.

Attempts to prepare larger quantities of the trioxide using methods published by others[27, 28] for rhenium trioxide have not been successful. Part of this difficulty is due to the fact that apparently the trioxide reacts with even trace quantities of water. It may also be that the trioxide is too unstable to allow accumulation of any but trace quantities of this material. A more thorough attempt to prepare this compound has not been made, however, and its characterization is still incomplete.

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(27) Nechamkin, H., Kurtz, A. N., and Hiskey, C. F., J. Am. Chem. Soc., 73, 2828 (1951).

(28) Melaven, A. D., Fowle, J. N., Brickell, W., and Hiskey, C. F., "Inorganic Synthesis", Vol. III, McGraw-Hill, New York, N. Y., 1950, p. 187.

G. Other Compounds of Technetium

Table III summarizes some of the other compounds which have been reported for technetium but which were not prepared in connection with this research. In general, those of Nelson and Parker involved hundred milligram quantities, while the others were characterized with quantities of a few milligrams or less.

TABLE III

SUMMARY OF KNOWN TECHNETIUM COMPOUNDS

Compound	Investigator	Color	Properties
Tc	This Research; Fried[a]	grey	Inert to HCl; oxid. by aqua regia, nitric acid; burns in O_2.
NH_4TcO_4	Fried	white	Density: 2.73; tetragonal; very soluble; relatively stable; sublimes at ca. 150°.
$KTcO_4$	Fried; Parker[b]	white	$K_{s.p.}$ = 0.44 at 27°, 0.14 at 7°.
$AgTcO_4$	Fried[a]	-	Identified by X-ray diffraction.
K_2TcCl_6	Nelson[c]	yellow	Hydrolyses in water; isomorphous with but larger cell than K_2ReCl_6.
TcO_2	Nelson; This Research	black	Inert; dissolves in strong oxid. agents; isomorphous with ReO_2.
Tc_2O_7	This Research	yellow	Deliquescent; stable up to B. P. (310°); dissolves readily in water to give pertechnic acid; not isomorphous with Re_2O_7.
$HTcO_4$	This Research	red	Strong acid in water; loses water at elevated temperatures; deliquescent.
Tc_2S_7	Rulfs and Meinke[d]	black	Not precipitated in very conc. acid solns.; carries excess sulfur.
TcS_2	Fried[a]	black	Prepared by heating Tc_2S_7 with excess sulfur; identified by X-ray diffraction.
TcO_3	This Research	red	Disproportionates in water; not definitely characterized

[a]Fried, S., Private communication to G. E. Boyd, 1950.

[b]Parker, G. W., Oak Ridge National Laboratory Chemistry Division Quarterly Report, ORNL-1116, 1951.

[c]Nelson, C. M., "The Magnetochemistry of Technetium and Rhenium", Doctoral Dissertation, The University of Tennessee, 1952.

[d]Rulfs, C. L., and Meinke, W. W., J. Am. Chem. Soc., 74, 235 (1952).

CHAPTER III

VAPOR PRESSURE STUDIES

A. The Vapor Pressure of Technetium Heptoxide

Technetium heptoxide was found in course of preparation to be volatile. It was of interest, therefore, to study its vapor pressure as a part of the characterization of this compound. Similar measurements have also been made on rhenium heptoxide[1] although manganese heptoxide is apparently too unstable to study in this manner.[2] Since loss of technetium had occurred in previous tracer experiments[3] when various solutions of technetium had been evaporated to dryness, it was of interest to see if this loss could be accounted for by the volatility of the heptoxide. This compound results on dehydrating acidic solutions of Tc(VII).

Technetium heptoxide, like rhenium heptoxide, is corrosive and is reduced by both mercury and organic vapors. An all-glass "sickle" or Bourdon gauge was therefore used (see Figures 3 and 4) for the measurements. The gauge was designed after one described by Phipps[4],

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(1) Smith, W. T., Jr., Line L., and Bell, W. A., J. Am. Chem. Soc., in press (1952).

(2) Mellor, J. W., "Treatise on Inorganic and Theoretical Chemistry", Vol. 12, Longmans, Green and Co., New York, N.Y., 1932, p. 466.

(3) Hackney, J. C., J. Chem. Ed., 28, 186 (1951).

(4) Phipps, T. E., Spealman, M. L., and Cooke, T. G., J. Chem. Ed., 12, 321 (1935).

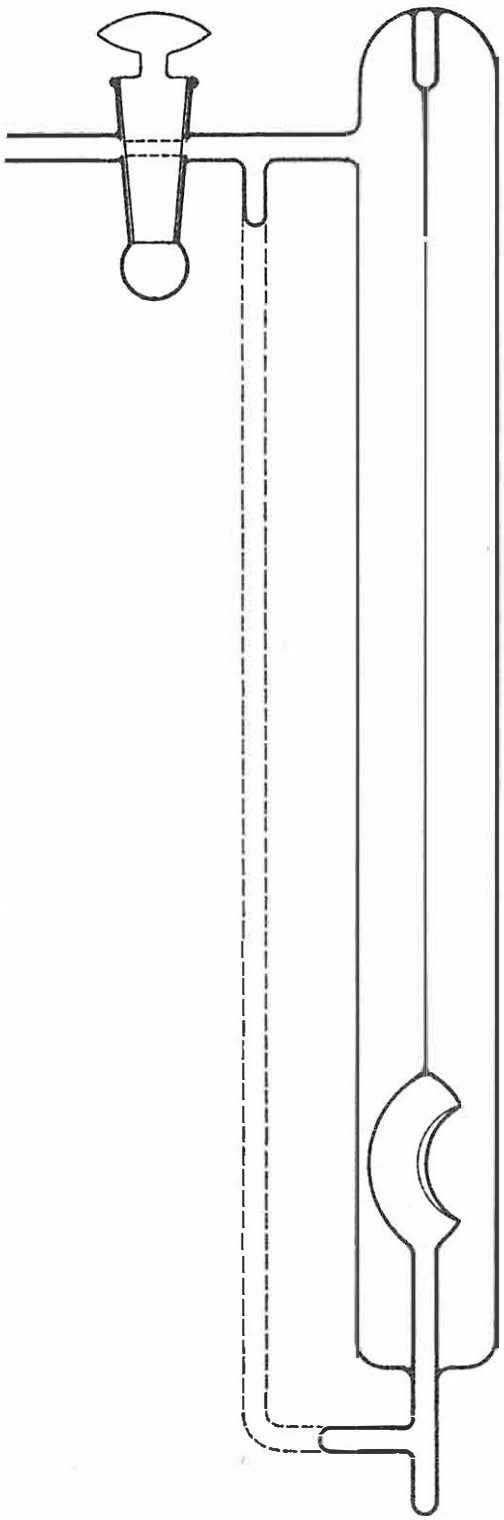


FIGURE 3.- SICKLE GAUGE

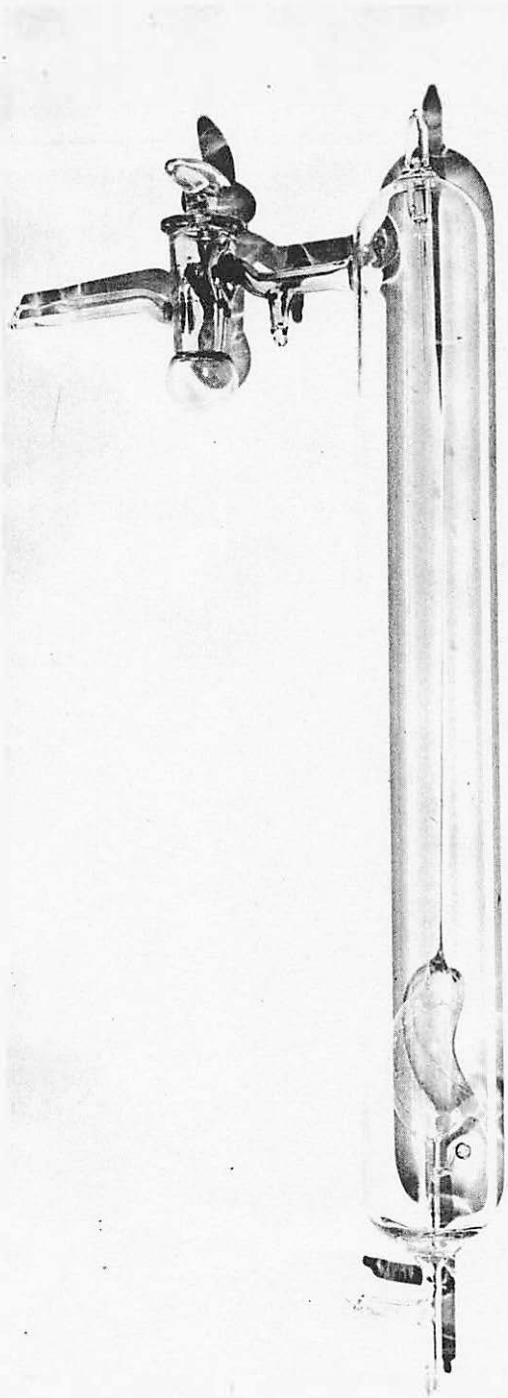


FIGURE 4.- SICKLE GAUGE

and similar to the one used by Smith.[5] It was used as a differential or as a null-point indicator for the vapor pressure of the liquid, and as an absolute manometer for the measurements on the solid heptoxide. The deflection was linear over a 2-3 mm. range, and its sensitivity was 1 mm. displacement/mm. pressure differential. A traveling microscope was used to read the relative displacement between a fixed, reference pointer and the index pointer. When used as a null instrument, the pressure in the gauge jacket necessary to return the pointer to its "zero" position was read on a closed tube mercury manometer with a cathetometer.

For the solid, which had an unexpectedly low vapor pressure, the jacket was evacuated to a known pressure which was held constant, and the relative displacement between the pointers was measured as a function of the temperature of the system. The gauge was then calibrated in an absolute manner with a McLeod gauge, using the sensitivity previously determined.

Zero-point corrections were determined by cooling the gauge to ice temperatures and determining the pressure required to "balance the gauge". These corrections were negligible at higher pressures, but at the pressures exerted by solid technetium heptoxide they amounted to 20 percent or greater. While some uncertainty was introduced thereby, a reasonable estimate of the vapor pressure of the solid could be made. The pressure readings were accurate to ± 0.05 mm. for the liquid and to ± 0.005 mm. for the solid. Temperature measure-

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(5) Smith, W. T., Jr., Line, L., and Bell, W. A., J. Am. Chem. Soc., in press, 1952.

ments were made with N. B. S. calibrated thermometers read to ± 0.1° and were corrected for immersion.

The gauge and its pressure jacket were rigidly suspended vertically in an oil-thermostat containing silicone oil.[6] This thermostat could be regulated continuously from below room temperature (by cooling coils) up to about 250°. (At the higher temperatures, p-aminophenol was added to prevent polymerization of the oil.) The average temperature control was somewhat better than ± 0.2°.

The pressure system used for maintaining and reading the pressure in the gauge jacket contained a 20 l. carboy as a damping device to minimize any sudden changes in the pressure of the system. The vapor pressure apparatus is shown in Figure 5.

No decomposition of technetium heptoxide was noticed during the vapor pressure measurements. This was in accord with previous experience which had indicated that the compound is stable even at its boiling point (310°).

There was no noticeable curvature to the line obtained when the data (Tables IV, V) were plotted as log P against 1/T. A least squares method was used, therefore, to obtain the two-term Clausius-Clapeyron equations:

$$\text{Solid-vapor:} \qquad \log P = -7205/T + 18.279 \qquad \text{(III-1)}$$

$$\text{Liquid-vapor:} \qquad \log P = -3571/T + 8.999 \qquad \text{(III-2)}$$

The probable error for the liquid was ± 1 per cent; for the solid, ± 8 per cent. Equilibrium values were insured by taking measurements

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(6) Type DC-550, obtained from the Dow Corning Corporation, Midland, Michigan.

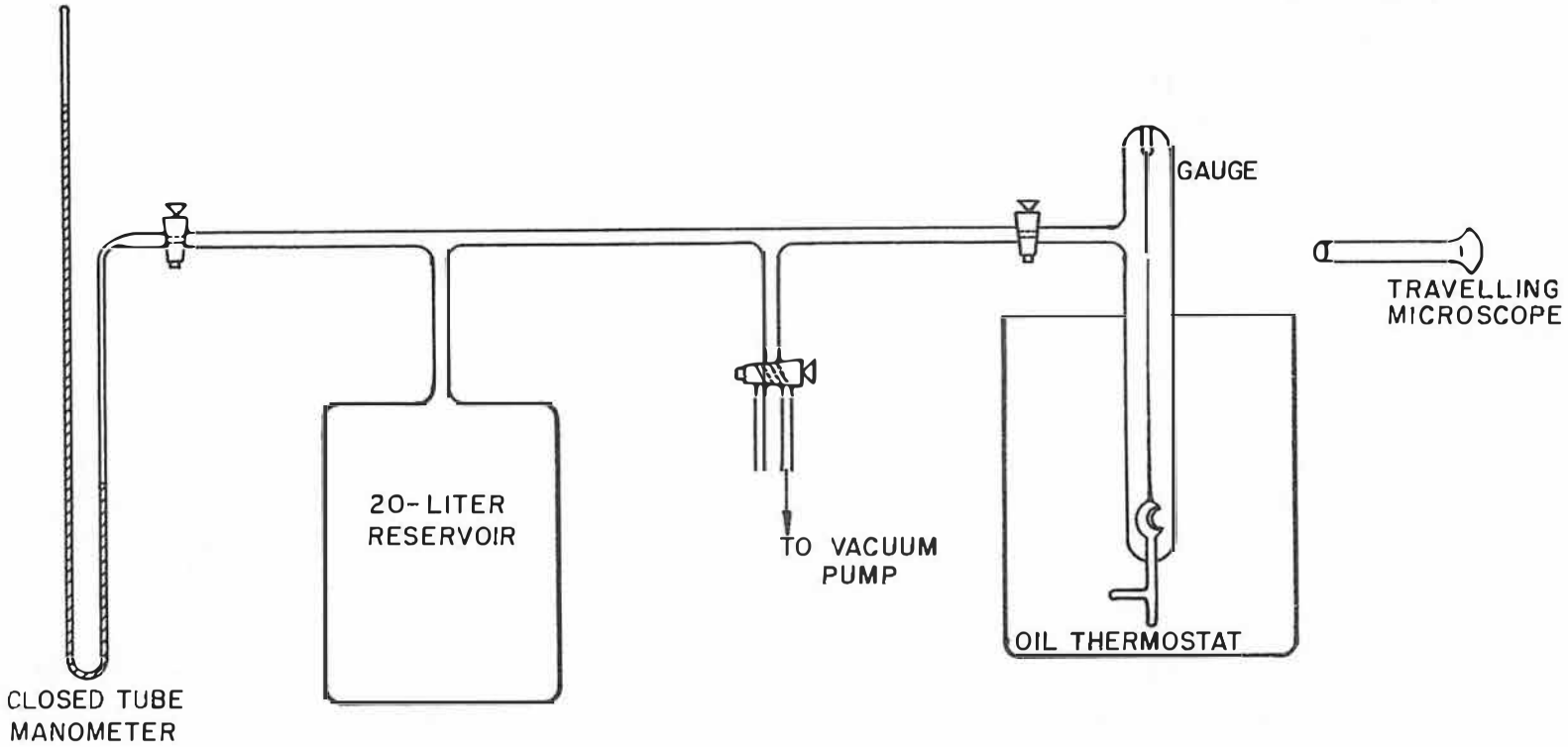


FIGURE 5.- VAPOR PRESSURE APPARATUS

TABLE IV

THE VAPOR PRESSURE OF SOLID TECHNETIUM HEPTOXIDE

$T^{a}_{obs.}$	$T_{corr.}$	$1/T \times 10^3$	$P^{b}_{obs.}$	$P_{corr.}$	$P^{c}_{calc.}$	$\triangle^{d}$
391.7	391.2	2.556	0.995	0.65	0.74	-0.09
389.2	388.7	2.573	0.700	0.46	0.55	-0.09
388.2	387.7	2.579	0.660	0.42	0.50	-0.08
384.6	384.1	2.604	0.720	0.36	0.33	0.03
379.0	378.5	2.642	0.400[e]	0.215	0.18	0.04
378.4	377.9	2.646	0.555	0.18	0.16	0.02
373.6	373.2	2.680	0.415	0.095	0.094	0.00
368.5	368.5	2.714	0.240[e]	0.05	0.05	0.00
363.0	362.2	2.761	0.300	0.03	0.03	0.00

[a]Degrees absolute.

[b]Millimeters of mercury.

[c]Calculated from equation III-1.

[d] $\triangle = P_{corr.} - P_{calc.}$

[e]Pressures so indicated obtained on cooling.

TABLE V

THE VAPOR PRESSURE OF LIQUID TECHNETIUM HEPTOXIDE

$T_{obs.}$[a]	$T_{corr.}$	$1/T \times 10^3$	$P_{obs.}$[b]	$P_{corr.}$	$P_{calc.}$[c]	Δ[d]
393.3[e]	393.3	2.543	0.50	1.0	0.8	0.2
413.6	413.1	2.421	1.60	2.1	2.3	-0.2
426.8	427.5	2.339	3.50	4.0[f]	4.4	-0.4
440.0	441.0	2.268	6.80	7.3	7.9	-0.6
445.3	446.4	2.224	9.10	9.6	10.0	-0.4
458.3	459.8	2.175	16.20	16.7[f]	17.1	-0.4
472.8	473.8	2.111	28.50	29.0	28.9	0.1
483.5	483.5	2.068	42.40	42.9[f]	41.1	1.8
489.7	489.7	2.042	54.10	54.6	50.9	3.7
503.0	503.0	1.988	82.40	82.9[f]	79.4	3.5
512.5	512.5	1.949	107.35	107.8	107.4	0.4
519.1	519.5	1.925	132.90	133.4[f]	133.4	0.0
521.0	521.5	1.918	141.40	141.9[f]	141.2	0.7
524.0	524.5	1.907	153.60	154.1	154.7	-0.6
528.7	529.4	1.889	176.70	177.2	179.2	-2.0

[a] Degrees absolute.

[b] Millimeters of mercury.

[c] Calculated from equation III-2.

[d] $\Delta = P_{corr.} - P_{calc.}$

[e] Triple point.

[f] Pressures so indicated obtained on cooling.

on both heating and cooling of the sample. The data are also plotted in Figure 6, along with those of Smith[7] for rhenium heptoxide. The thermodynamic quantities that can be calculated from the vapor pressure equations above are given in Table VI, along with the corresponding values for rhenium heptoxide.

As was expected from the similar atomic radii of technetium and rhenium[8] as well as the isomorphous nature of pertechnetate and perrhenate ions[9], the heats of fusion and vaporization of the two heptoxides were found to be very similar. The most surprising observation is the fact that technetium heptoxide melts at such a low temperature, and remains liquid over a wide temperature range. This also is evidenced by the very large entropy of fusion, which appears to be higher than that recorded for any other compound.[10] The fact that technetium heptoxide solid is electrically conducting at temperatures near the melting point is not in conflict with this high entropy change. The reasons for the apparent non-conductance of the liquid state are, at present, unknown. Apparently, then, the entropy change must either be associated with this conductivity or due to a restricted rotation in the solid state with "unfreezing" of the rotational entropy

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(7) Smith, W. T., Jr., Line, L., and Bell, W. A., J. Am. Chem. Soc., in press (1952).

(8) Mooney, Rose C. L., Acta Cryst., 1, 161 (1948).

(9) Zachariasen, W. H., Oak Ridge National Laboratory Memo., CF-47-11-464 (1947).

(10) Kelley, K. K., U. S. Bur. Mines Bull., 393, 134 (1936).

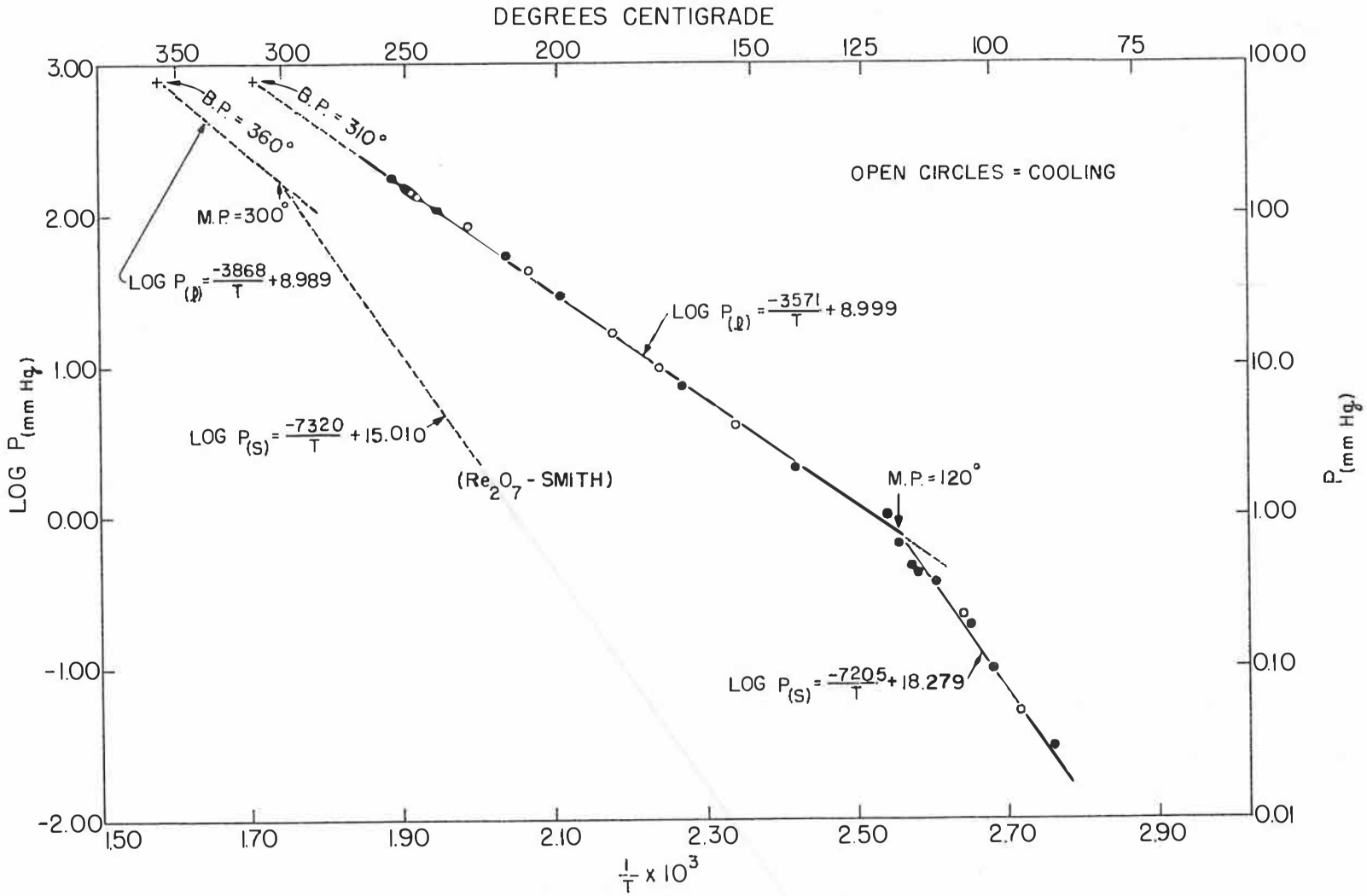


FIGURE 6.- VAPOR-PRESSURE OF TECHNETIUM HEPTOXIDE

TABLE VI

COMPARISON OF THERMODYNAMIC PROPERTIES OF TECHNETIUM AND RHENIUM HEPTOXIDES

	Tc_2O_7 [a]	Re_2O_7 [b]
$\Delta F^{c}_{subl.}$	32,950 - 70.4 T	33,500 - 55.6 T
$\Delta F_{vap.}$	16,330 - 28.0 T	17,700 - 28.0 T
$\Delta F_{fus.}$	16,620 - 42.4 T	15,810 - 27.6 T
$\Delta H^{d}_{fus.}$	16.6 ± 0.5	15.8 ± 0.1
$\Delta H_{vap.}$	16.3 ± 0.2	17.7 ± 0.1
$\Delta S^{e}_{fus.}$	42 ± 2	27.6 ± 0.2
$\Delta S_{vap.}$	28.0 ± 0.3	28.0 ± 0.1
M.P.	120 ± 1°	300 ± 1°
B.P.[f]	310 ± 1°	360 ± 1°

[a]Calculated from equations III-1 and III-2.

[b]From the data of Smith, W. T., Jr., Line, L., and Bell, W. A., J. Am. Chem. Soc., in press (1952).

[c]Calories $mole^{-1}$.

[d]Kcal. $mole^{-1}$.

[e]Calories $mole^{-1}$ $degree^{-1}$.

[f]Calculated from vapor pressure equation.

on fusion. The complete understanding of this phenomenon must await absolute entropy determinations, more accurate conductivity, density and crystallographic measurements on the heptoxide.

B. The Vapor Pressure of Pertechnic Acid

The vapor pressure of pertechnic acid was run, in a manner similar to that described above, to determine its stability. The compound was prepared in situ by distilling technetium heptoxide into the lower part of the gauge and then letting water vapor into the vacuum line. The oxide immediately became moist and the excess water was pumped out by warming the compound slightly. Samples prepared in this manner contained some excess technetium heptoxide, but the amounts were so adjusted that enough acid was left to give equilibrium pressures of water vapor.

The dissociation equilibrium can be written:

$$HTcO_4(s) = \tfrac{1}{2} H_2O_{(v)} + \tfrac{1}{2} Tc_2O_7(s) \qquad \text{(III-3)}$$

The vapor pressure data for this dissociation are given in Table VII, and are shown in Figure 7 along with similar data for perrhenic acid by Smith.[11] They were fitted to a two term Clausius-Clapeyron equation for the reaction given by equation (III-3):

$$\log P = -2409/T + 8.201 \qquad \text{(III-4)}$$

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(11) Smith, W. T., Jr., Line, L., and Bell, W. A., J. Am. Chem. Soc., in press, (1952).

TABLE VII

THE DISSOCIATION PRESSURE OF PERTECHNIC ACID

$T^{a}_{obs.}$	$T_{corr.}$	$1/T \times 10^{3}$	$P^{b}_{obs.}$	$P_{corr.}$	$P^{c}_{calc.}$	$\triangle^{d}$
291.5	291.8	3.427	3.00[e]	1.00	1.00	0.00
305.5	305.7	3.271	4.40[e]	2.40	2.37	0.03
313.7	313.8	3.187	5.80[e]	3.80	3.77	0.03
322.3	322.4	3.102	7.95	5.95	6.01	-0.06
330.5	330.6	3.025	11.10[e]	9.10	9.20	-0.10
337.0	337.2	2.966	15.10	13.20	12.74	0.56
341.4	341.5	2.928	17.45	15.45	15.70	-0.25
347.4	347.5	2.878	22.80[e]	20.80	20.69	0.11
353.6	353.8	2.827	29.30	27.30	27.15	0.15
363.3	363.3	2.753	43.45[e]	41.45	41.22	0.23

[a]Degrees absolute.

[b]Millimeters of mercury.

[c]Calculated from equation III-4.

[d]$\triangle = P_{corr.} - P_{calc.}$

[e]Pressures so indicated obtained on cooling.

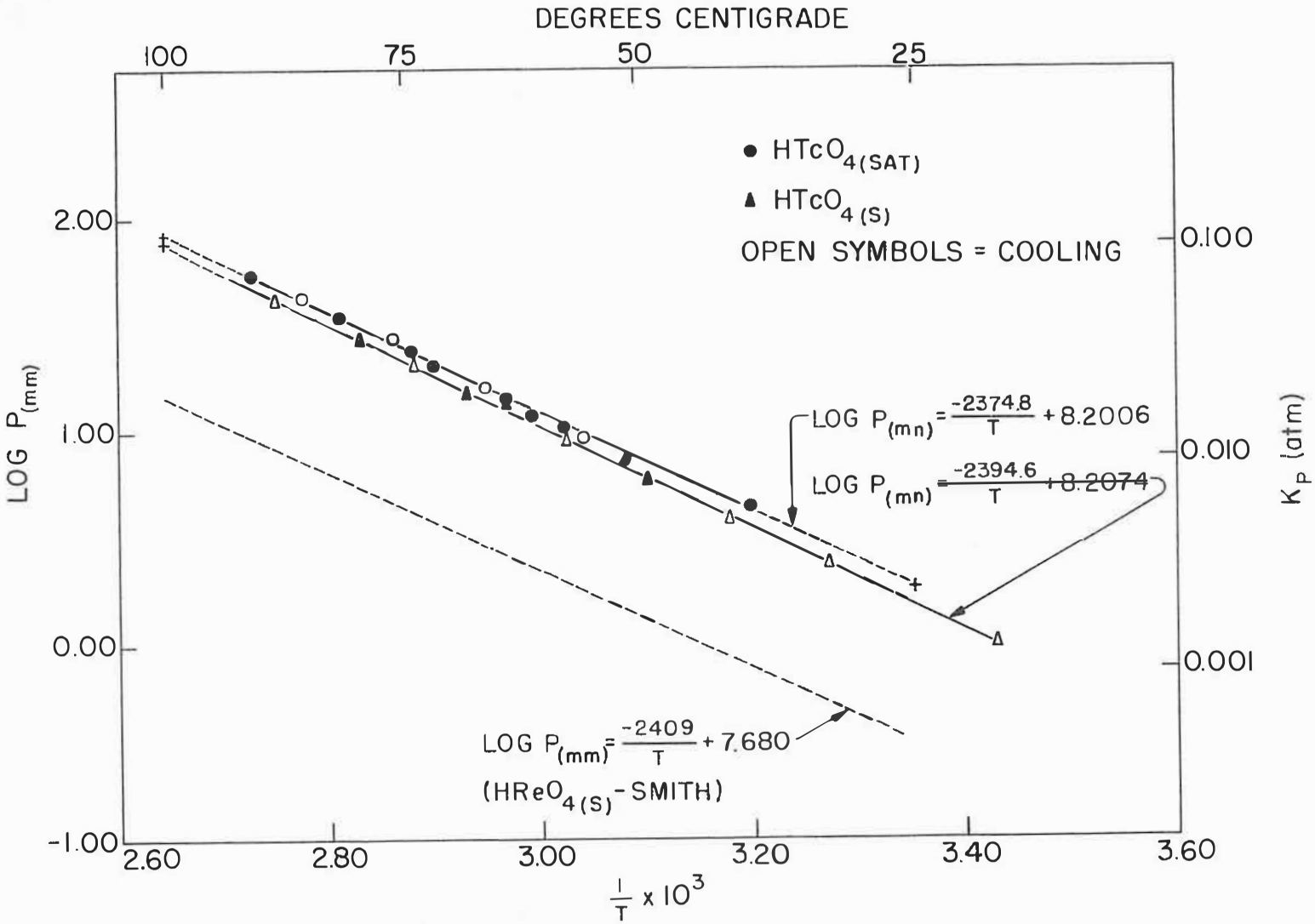


FIGURE 7.- VAPOR PRESSURE OF H_2O OVER $HTcO_{4(S)}$ AND $HTcO_{4(SAT)}$

The vapor pressure of $Tc_2O_7(s)$ itself was negligible at these temperatures. It can be seen that the acid is more unstable with respect to its loss of water than is perrhenic acid. An evaporation of an acidic solution of Tc(VII) at water bath temperatures would soon give the anhydrous oxide. Continued heating at 100° would eventually give rise to loss of the heptoxide which has a vapor pressure of about 0.6 mm. at this temperature. Hence, this type of procedure for concentration of technetium solutions is to be avoided except in basic media.

By subtracting the heat of vaporization for water[12] from equation (III-3) above, we can write:

$$HTcO_4(s) = \tfrac{1}{2} H_2O(l) + \tfrac{1}{2} Tc_2O_7(s) \qquad \text{(III-5)}$$

The thermodynamic quantities which can be calculated from the data for equations (III-3) and (III-5) are given in Table IX.

C. The Vapor Pressure over Saturated Pertechnic Acid Solutions

The vapor pressure of water in equilibrium with saturated pertechnic acid solutions was also determined in the same manner as for anhydrous pertechnic acid. Technetium heptoxide was allowed to absorb enough water to give rise, visibly, to solution in contact with the solid pertechnic acid. The vaporization equation can be written:

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(12) National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties", Series I, 1948.

$$HTcO_4(sat) = HTcO_4(s) + H_2O_{(v)} \qquad (III-6)$$

The data were fitted as before to the equation:

$$\log P = -2375/T + 8.201 \qquad (III-7)$$

By subtracting the vaporization for water, the thermodynamic functions for the following reaction can be calculated:

$$HTcO_4(sat) = HTcO_4(s) + H_2O_{(l)} \qquad (III-8)$$

The thermodynamic data for this system are given in Table IX , and the vapor pressure data in Table VIII and Figure 7. The vapor pressures of the saturated solution are only a few mm. higher than for the anhydrous acid. Since the free energy difference between the solid acid and the saturated solution is given by:

$$\Delta F = -RT \ln P_{sat}/P_{solid} \qquad (III-9)$$

it is seen that there is very little tendency for the system technetium heptoxide-water to add additional water after once forming the anhydrous pertechnic acid. Corresponding measurements for saturated perrhenic acid have not been made; presumably the situation here would be very similar.

TABLE VIII

THE VAPOR PRESSURE OF WATER OVER SATURATED PERTECHNIC ACID SOLUTIONS

T[a]	$T_{corr.}$	$1/T \times 10^3$	$P_{obs.}$[b]	$P_{corr.}$	$P_{calc.}$[c]	Δ[d]
312.6	312.9	3.196	6.40	4.40	4.08	0.32
324.3	324.5	3.082	9.23	7.23	7.61	-0.38
329.2	329.1	3.039	11.35[e]	9.35	9.63	-0.28
330.5	330.6	3.025	12.65	10.65	10.40	0.25
334.3	334.2	2.992	13.80	11.80	12.45	-0.65
337.1	337.0	2.967	16.15	14.15	14.28	-0.13
339.6	339.5	2.946	18.10[e]	16.10	16.01	0.09
344.8	344.7	2.901	22.05	20.05	20.48	-0.43
344.8	344.6	2.902	22.30	20.30	20.36	-0.06
347.7	347.5	2.878	25.25	23.25	23.22	0.03
351.1	351.0	2.849	29.60[e]	27.60	27.22	0.38
355.9	355.8	2.811	35.50	33.50	33.49	0.01
357.1	357.2	2.800	38.10[e]	36.10	35.58	0.52
361.1	361.0	2.770	44.35[e]	42.35	41.92	0.43
363.5	363.6	2.750	49.15[e]	47.15	46.78	0.37

[a]Degrees absolute.

[b]Millimeters of mercury.

[c]Calculated from equation III-7.

[d]$\Delta = P_{corr.} - P_{calc.}$

[e]Pressures so indicated obtained on cooling.

TABLE IX

THERMODYNAMIC DATA FOR SOLVATION REACTIONS OF TECHNETIUM AND RHENIUM HEPTCXIDES

Reaction	$\triangle H^{a}_{25^o}$	$\triangle F^{o}_{25^o}$	$\triangle S^{b}_{25^o}$
$2HTcO_4(s) = Tc_2O_7(s) + H_2O^{c}_{(v)}$	10,950 ± 50	3686 ± 18	24.4 ± 0.2
$2HTcO_4(s) = Tc_2O_7(s) + H_2O^{d}_{(l)}$	430 ± 50	1632 ± 18	-4.0 ± 0.2
$HTcO_4(sat) = HTcO_4(s) + H_2O^{e}_{(v)}$	10,860 ± 100	3605 ± 18	24.3 ± 0.4
$HTcO_4(sat) = HTcO_4(s) + H_2O_{(l)}$	340 ± 100	1551 ± 18	-4.1 ± 0.4
$2HReO_4(s) = Re_2O_7(s) + H_2O^{f}_{(v)}$	11,020 ± 100	4460 ± 18	22.0 ± 0.4
$2HReO_4(s) = Re_2O_7(s) + H_2O_{(l)}$	500 ± 100	2418 ± 18	-6.4 ± 0.4

[a]Calories.

[b]Calories degree^{-1}.

[c]Calculated from equation III-4.

[d]Data for vaporization of water from Kelley, K. K., United States Department of the Interior, Bureau of Mines Bulletin 383, 1935, p. 51.

[e]Calculated from equation III-7.

[f]Calculated from data of Smith, W. T., Jr., Line, L. and Bell, W. A., J. Am. Chem. Soc., in press (1952).

CHAPTER IV

CALORIMETRY

A. The Heat of Combustion of Technetium Metal

One of the most fundamental thermochemical measurements which can be made on technetium is its heat of combustion in oxygen to give technetium heptoxide. The heats of formation of technetium heptoxide and aqueous pertechnic acid can be calculated from such measurements together with heats of solution and dilution. Similar measurements have been made on rhenium by Roth and Becker.[1] These authors found it necessary to burn the metal with a paraffin oil accelerator, as the combustion process would not proceed rapidly to completion otherwise. The same procedure has been used successfully with technetium.

The calorimeter (see Figures 8 and 9) consisted of a one liter glass dewar fitted to receive a combustion bomb and contained water as the calorimeter medium. The temperature rise was measured with a calibrated, glass-enclosed platinum resistance thermometer. A top cover plate containing a rubber O-ring was bolted onto a flanged copper ring cemented to the dewar, thus providing a water-tight seal. Three vertical copper tubes pierced the cover plate to allow entrance of a resistance thermometer, glass stirring rod and ignition wire

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(1) Roth, W. A., and Becker, G., Z. physik. Chem., A159, 27 (1932).

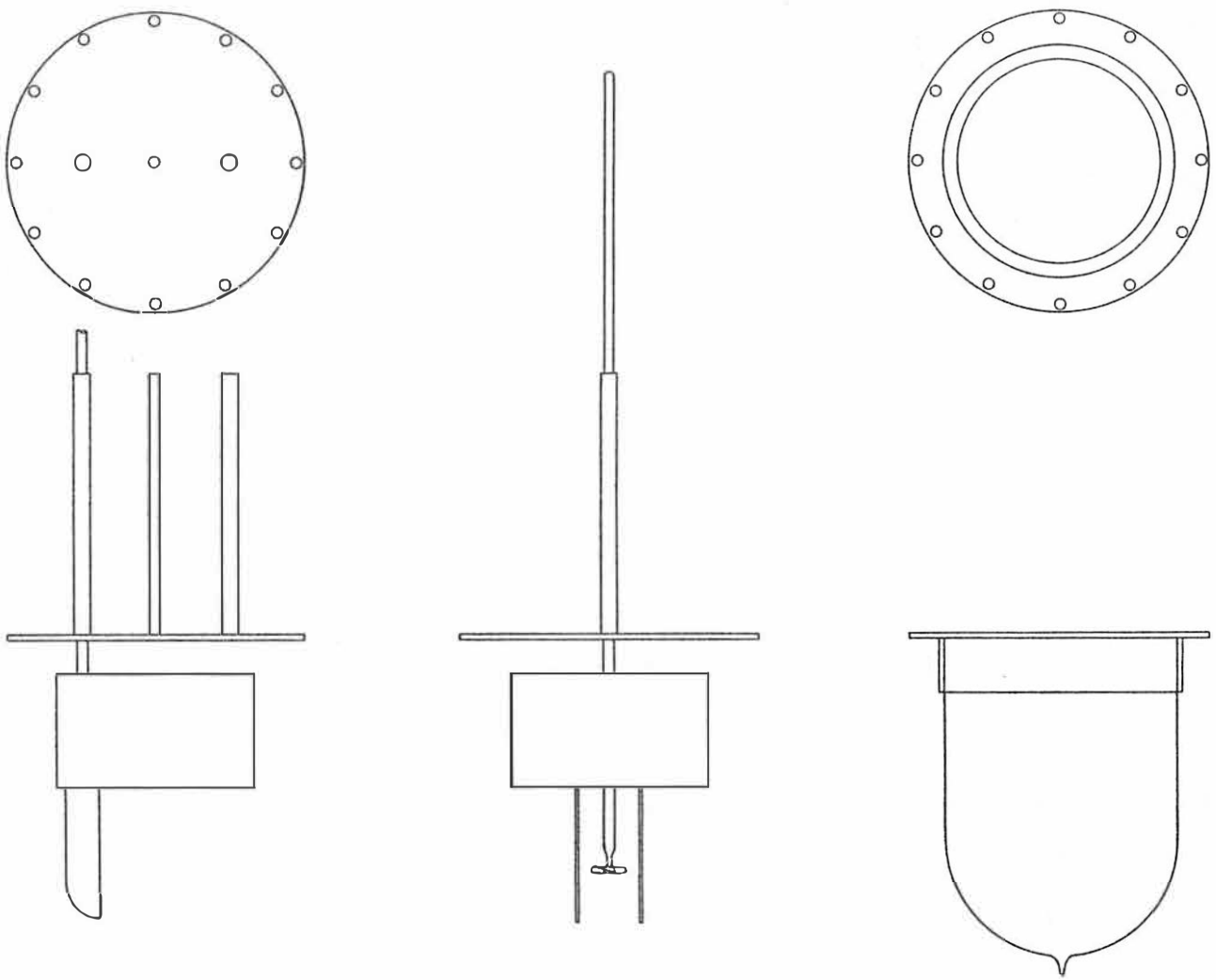


FIGURE 8.- COMBUSTION CALORIMETER

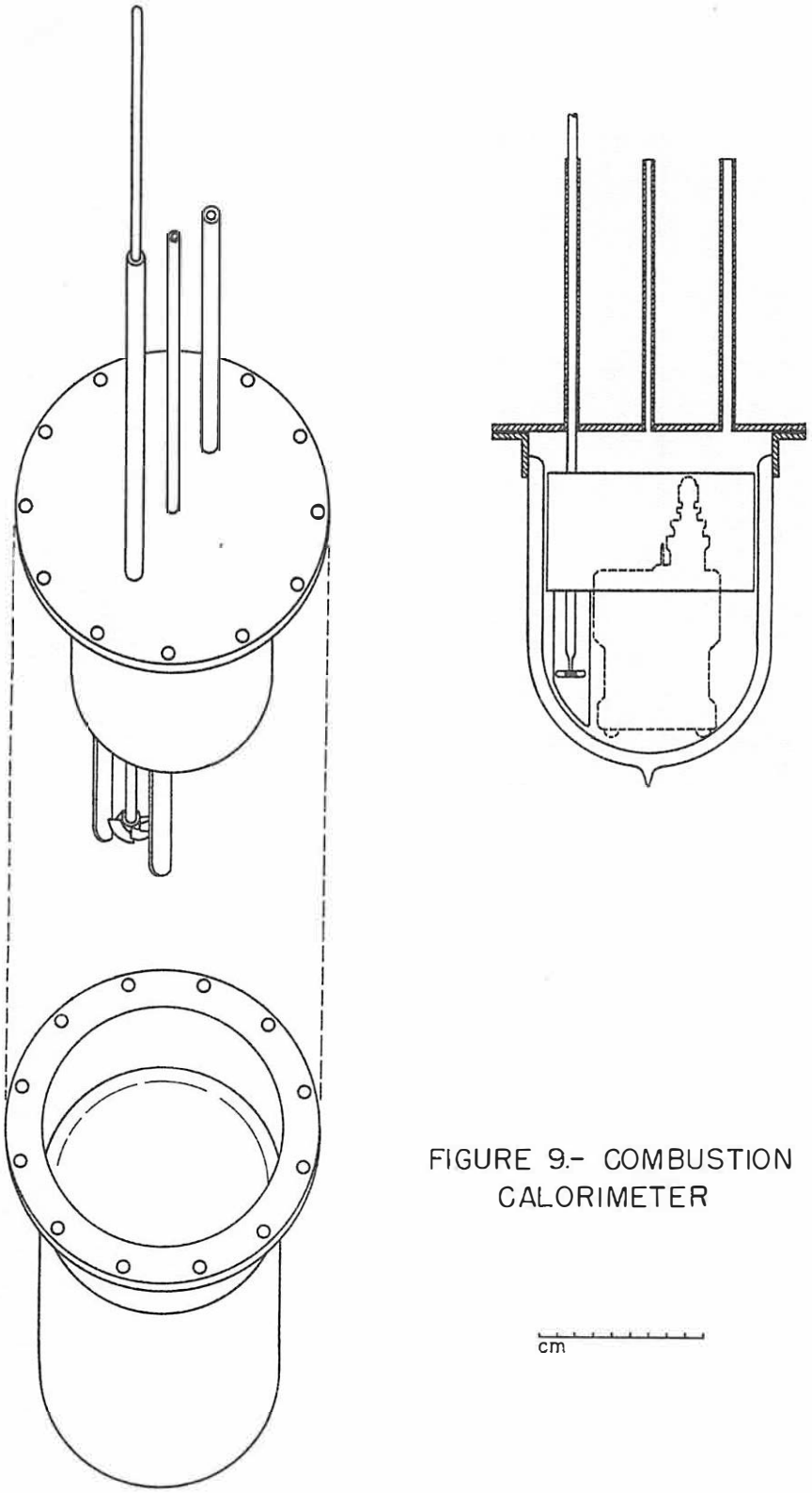


FIGURE 9.- COMBUSTION CALORIMETER

into the calorimeter. With such an arrangement, the whole assembly could be submerged in a constant temperature bath.

The combustion bomb (see Figure 10) was one commercially available from the Parr Instrument Company. It was of the semi-micro type, containing an inlet-outlet valve and two ignition terminals. It was constructed out of a cobalt, nickel, steel alloy, and the internal volume was 50 ml. The bomb was suspended in the calorimeter by strings attached to the cover plate.

The sample to be burned was placed in a small quartz cup held in a platinum wire ring suspended from the bomb head. The dewar was filled by weighing in the proper quantity of water. To insure a constant heat-leak from the calorimeter, a radiation shield was also provided. This shield consisted of an inverted copper cup which fitted snugly into the dewar confining the heat leak between two copper surfaces about 2 cm. apart. This design is in accord with the recommendations of White.[2] The shield contained holes for the thermometer, stirrer, ignition wire and strings. Hanging vertically from the shield were two copper fins which served to provide two sides of a stirring channel, with the bomb and dewar forming the other two sides. A brass propeller on the end of a glass rod was centered in this channel and provided for the rapid mixing of the water. The propeller was rotated at 1500 r. p. m. by a synchronous motor. In order to cover the sensitive volume of the platinum resistance thermometer, it was

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(2) White, W. P., "The Modern Calorimeter", Chem. Catalog Co., New York, N. Y., 1928, p. 169.

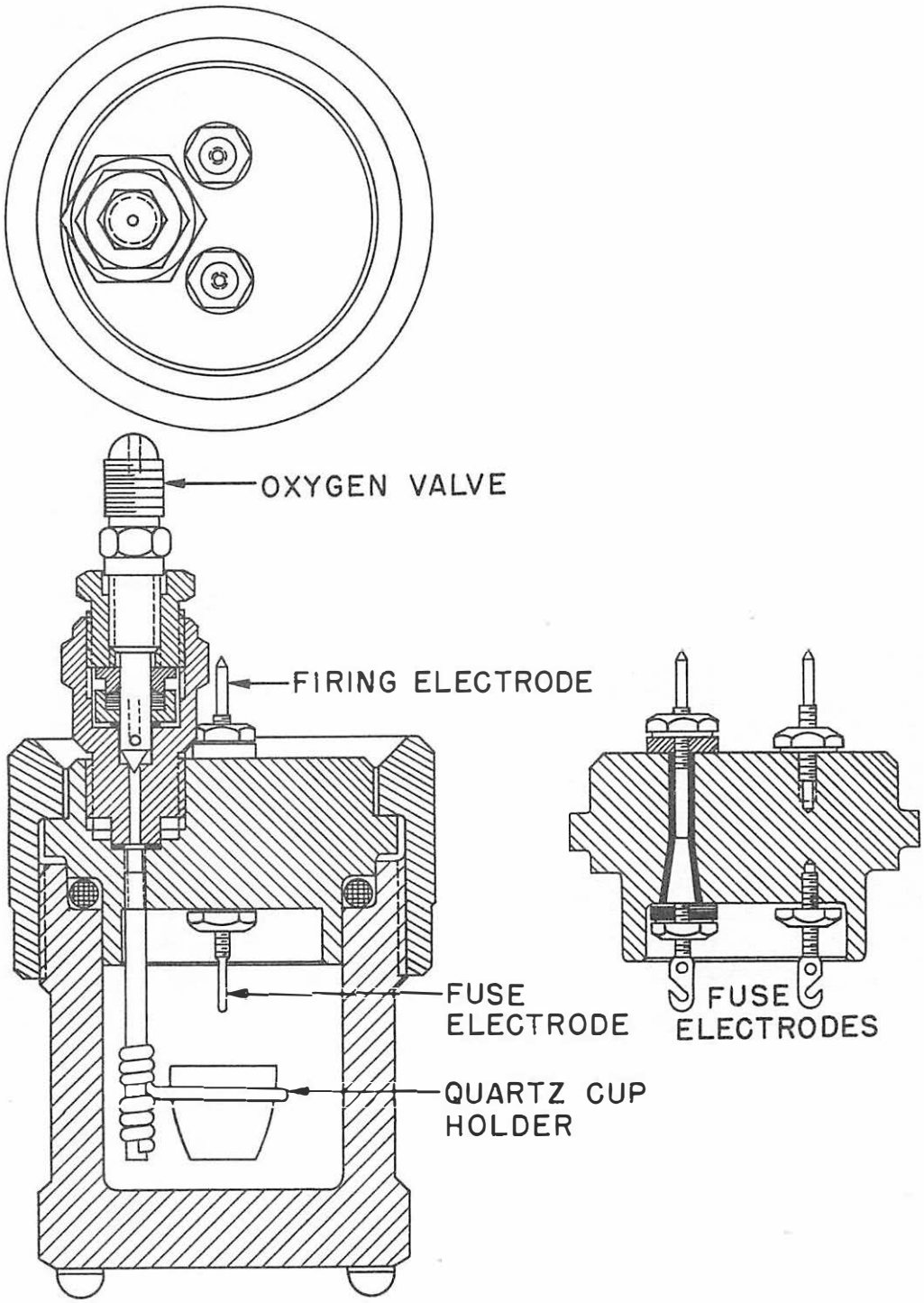


FIGURE 10.-
MICRO COMBUSTION BOMB

immersed about 2 cm. into the calorimeter medium.

The calorimeter assembly was totally submerged in a water thermostat bath at 25° which was regulated to ± 0.002°. The heat leak of the calorimeter to the bath was about 25 micro-deg. $sec.^{-1}$ $deg.^{-1}$. The stirrer also introduced a constant heat input of about 25 micro-deg. $sec.^{-1}$. The water accounted for 73.3 per cent of the total heat capacity of the calorimeter.

The temperature rise was determined by measuring the change in resistance of the platinum resistance thermometer with a Mueller bridge. Resistances were read to ± 0.00005 ohms, corresponding to about ± 0.0005°. The temperature rise of the calorimeter was determined by the Dickinson method[3] whereby the temperature difference between the two extrapolated flat portions of the temperature-time curve is taken at that time which corresponds to 0.6 of the total temperature rise. (See Appendix III, Figure 15). The average temperature of the combustion measurements was taken as the absolute temperature at the 0.6 time. Since this average temperature was within a half degree of 25° in all cases, all of the heats are referred to 25°. Uncertainties caused by this assumption are negligible.

Quantities ranging up to 100 mg. of technetium metal prepared by ammonium pertechnetate reduction were burned together with 50 mg. of paraffin oil. The combustion oxygen pressure was 30 atm. The mixture was ignited using a platinum wire over which a measured length

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(3) Dickinson, H. C., Natl. Bur. Standards Bull., 11, 189 (1914).

of a cotton thread fuse was hung, resting on the oil-metal combustion charge.

To ignite the mixture, a pulse of current was sent through the wire, and, although it was not sufficient in itself to melt the wire, the additional heat from the fuse did so in a fraction of a second (ca. 0.2 sec.). The heat input of the ignition process was determined by separate experiments.

The nitric acid, always formed from traces of nitrogen in the oxygen used, amounted to 0.0131 m.e., corresponding to a temperature rise of 0.00016°.[4] Since this same amount of acid was always formed regardless of the size of the oil charge, it was assumed that this corresponded to the amount of acid also formed in the oil-technetium burning. The fuse and nitric acid correction was $0.0047 \pm 0.0001^{\circ}$. The heat of combustion of the oil itself was determined by many separate experiments (See Table X). The standard deviation reported for the values in this chapter are calculated from the equation $S = \sqrt{\frac{\sum(\Delta x)^2}{n(n-1)}}$ where $\sum(\Delta x)^2$ represents the sum of the squares of the deviation of each determination from the average of n determinations. This error function has been recommended for calorimetry[5] and is in common use today. For a precision of the order of a few-hundredths of one percent, it would have been necessary

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(4) Washburn, E. W., J. Research Nat. Bur. Standards, 10, 525 (1933).

(5) Rossini , F. D., and Deming, W. E., J. Wash. Acad. Sci., 29, 416 (1939).

TABLE X

HEAT OF COMBUSTION OF PARAFFIN OIL ACCELERATOR

ΔR	ΔT	$\Delta T_{corr.}$[a]	Sample Wt.	Temperature Rise per g.
0.05840Ω	0.5420°	0.5373°	68.66 mg.	7.826 deg. $g.^{-1}$
0.05810	0.5400	0.5353	68.32	7.835
0.08829	0.8183	0.8136	103.00	7.996
0.12234	1.1381	1.1334	142.42	7.958
0.05163	0.4798	0.4751	59.89	7.933
0.06820	0.6344	0.6297	79.54	7.917
0.08334	0.7745	0.7698	97.65	7.884
0.07950	0.7395	0.7348	92.77	7.921
0.08941	0.8302	0.8255	104.20	7.922
			Average[b]:	7.910 ± 0.018 deg. $g.^{-1}$

[a]Corrected for fuse ignition and nitric acid formation

[b]This corresponds to a heat of combustion (not reduced to standard state conditions) of 11.04 kcal. g^{-1}.

to correct each of the oil combustions by the Washburn corrections[6] to standard state conditions. However, since the maximum precision of this calorimeter (because of its necessarily small design) was only about 0.2 percent, these corrections were not significant.

The heat capacity of the calorimeter was determined by combustion of samples of benzoic acid provided by the Bureau of Standards for this purpose (Sample 39f). (See Table XI.) In this case, the Washburn[7] corrections, although small, were made. Thus, the standard heat of combustion of the acid sample was quoted to be 26.4284 international kilojoules $g.^{-1}$; corrected this became 26.4279 int. kj. $g.^{-1}$, or 6,316.42 defined[8] cal. $g.^{-1}$. Using 4.521 deg. $g.^{-1}$ from Table XI, we calculate the heat capacity of the calorimeter to be 1397.1 cal. $deg.^{-1}$ at 25°.

In the case of the technetium-oil mixtures, two corrections were made. First, the temperature rise caused by the ignition process was subtracted (0.0047°), and second, the rise due to the amount of oil used was subtracted. As in the case of the combustion of pure oil alone, the Washburn corrections should also be applied for both the technetium and oil. However, since the oil and technetium were burned under the same conditions as the oil alone, these corrections

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(6) Washburn, E. W., loc. cit.

(7) Washburn, E. W., loc. cit.

(8) See Appendix, Part II, for a list of the physical constants used in calculations in this dissertation.

TABLE XI

BENZOIC ACID COMBUSTION CALIBRATION

$\triangle R$	$\triangle T$	$\triangle T_{corr.}^{(a)}$	Sample Wt.	Temperature Rise per g.
0.06330Ω.	0.5891°	0.5844°	128.86 mg.	4.535 deg. $g.^{-1}$
0.03632	0.3370	0.3324	73.72	4.509
0.05646	0.5237	0.5190	114.68	4.526
0.05914	0.5489	0.5442	120.53	4.515
			Average:	4.521 ± 0.006 deg. $g.^{-1}$

[a]Corrected for fuse ignition and nitric acid formation.

were negligible. The combustion data for technetium-oil mixtures and the resulting corrections to obtain the heat of combustion at constant volume of technetium are given in Table XII. It should be noted that these data are for conditions existing in the bomb, and further, that corrections must be made to obtain the true standard state enthalpy of combustion.

The technetium heptoxide from the technetium combustion would have dissolved in the water formed from the combustion of the oil to give a concentrated solution of pertechnic acid. Because of the limited quantities of technetium available, heat of dilution studies could not be made on these relatively concentrated solutions. Therefore, 2.00 additional ml. of water was placed in the bomb so that the final product of the combustion was a more dilute solution of pertechnic acid. This solution was then used for heat of dilution studies which are reported in a later section of this chapter.

From Table XII, we obtain for the bomb heat 0.998 deg. $g.^{-1}$. Using a heat capacity for the calorimeter (from page 47) of 1397.1 cal. $deg.^{-1}$, and an atomic weight for technetium of 98.91[9], we obtain for the actual bomb process:

$$2\,Tc(s) + 7/2\,O_2(g,\ 30\ atm.) + H_2O_{(l)} + aq. = 2HTcO_4(0.3\ \underline{M}.) \qquad \Delta E' = -276.0 \pm 2.8\ kcal. \qquad (IV\text{-}1)$$

(9) See Appendix II for the value used for the atomic weight of technetium in this research.

TABLE XII

HEAT OF COMBUSTION OF TECHNETIUM METAL

$\triangle R$	$\triangle T$	$\triangle T_{(corr.)}$[a]	Wt. Oil	$\triangle T_{(Oil)}$	$\triangle T_{(net)}$	Wt. Tc[b]	Temperature Rise per g.
0.07150 Ω	0.6645°	0.6598°	79.56 mg.	0.6293°	0.0305°	31.01 mg.	0.983 deg. $g.^{-1}$
0.08422	0.7834	0.7787	94.83	0.7501	0.0286	29.25	0.979
0.09801	0.9117	0.9070	107.44	0.8499	0.0572	56.39	1.014
0.12368	1.1526	1.1479	135.26	1.0699	0.0780	76.25	1.023
0.06718	0.6244	0.6197	72.78	0.5757	0.0440	45.38[c]	0.969
0.13433	1.2492	1.2445	144.60	1.1438	0.1007	99.00[c]	1.018
						Average:	0.998 ± 0.009 deg. $g.^{-1}$

[a]Corrected for fuse ignition and nitric acid formation.

[b]Weight of technetium metal actually burned; this represents 80 - 90 percent of the initial charge.

[c]Samples so indicated had been degassed at 800° for 2 - 3 hours in vacuum.

The concentration of 0.3 M. represents the average concentration for the six experiments given in Table XII. Since there was no noticeable trend in the heat of reaction as a function of the amount of metal burned, it was concluded that the differences in concentration of pertechnic acid solutions formed did not contribute any significant error.

It was found that 80-90 percent of the technetium metal in the charge was burned, and that the residue left in the ignition cup was pure technetium metal. This observation was checked by determining the actual amount of technetium present as pertechnic acid in the bomb solution. The average distribution of technetium was as follows: on the bomb head, 10 percent; on the bomb walls, 5 percent; in the bomb solution, 85 percent. Since most of the technetium was found in the bomb solution, the average concentration of this solution will be taken as the average concentration of the pertechnic acid formed in equation (IV-1).

Two of the samples of technetium metal were thoroughly degassed at high temperatures in a vacuum following their preparation from ammonium pertechnetate by hydrogen reduction. Since the heats of combustion of these two samples were, within the experimental error, the same as for the other, non-degassed samples, it may be concluded that technetium prepared in this manner does not contain hydrogen to any appreciable extent.

To correct equation IV-1 to standard state conditions, a heat term for the change of pressure from 30 atm. to unit fugacity must be added:

$$7/2\ O_2(g\ ,\ \text{unit fugacity}) = 7/2\ O_2(g\ ,\ 30\ \text{atm.}) \qquad \text{(IV-2)}$$

Taking $(\partial E/\partial P)_{25^\circ}$ equal to -6.5 joules atm.$^{-1}$ mole^{-1} for the compression[10], we obtain 0.68 kilo-joules or 0.16 kcal. for equation IV-2. Hence:

$$2\ Tc(s) + H_2O_{(l)} + 7/2\ O_2(g\ ,\ \text{unit fugacity}) + \text{aq.} = 2HTcO_4(0.3\ \underline{M}.) \qquad \text{(IV-3)}$$
$$\triangle E = -276.2 \pm 2.8\ \text{kcal.}$$

(The heat of dilution of 0.3 M. pertechnic acid solution to infinite dilution will be described in a later section of this chapter.)

Since the actual energy measured for the bomb process corresponds to a change in E, we must add to this the PV work done to obtain the enthalpy change:

$$\triangle H = \triangle E + \triangle nRT \qquad \text{(IV-4)}$$

Taking $\triangle n$ as -7/2, $\triangle nRT$ has the value of -2.1 kcal. The heat of formation for the pertechnic acid solution then becomes:

$$2Tc(s) + H_2O_{(l)} + 7/2\ O_{2(g)} = 2HTcO_4(0.3\ \underline{M}.) \qquad \text{(IV-5)}$$
$$\triangle H = -278.3 \pm 2.8\ \text{kcal.}$$

The heats of combustion of rhenium metal and rhenium trioxide have also been determined. The data for rhenium can then be compared

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(10) Rossini, F. D., and Frandsen, M., J. Research Nat. Bur. Standards, 9, 733 (1932).

with the heat of combustion of the metal and ReO_3 determined by Roth and Becker[11] as a check on the accuracy of the experimental method. These data and the comparison are given in Appendix IV.
The agreement is satisfactory for rhenium metal, but not in agreement with their value for ReO_3. Since this later value was determined only indirectly, it is felt that the value determined in this research by direct oxidation is more accurate.

B. The Heat of Solution of Technetium Heptoxide

Since it was necessary to use oil to produce a satisfactory combustion of technetium metal samples, the final state of the technetium was that of an aqueous solution of the oxide, i.e., a solution of pertechnic acid. Before the heat of formation of the oxide can be determined, therefore, it is necessary to know the heat of solution of the oxide to give the same concentration of acid as that resulting from the combustion (0.3 M.). An alternative procedure would be to determine the heat of solution of the anhydrous oxide at infinite dilution, and the heat of dilution of the bomb solution to infinite dilution.

The solution calorimeter was constructed from a small cylindrical dewar (see Figure 11) $5\frac{1}{4}$ inches long and $1\frac{1}{2}$ inches in diameter. It was fitted with a standard taper joint so that a glass stoppered top could be fitted onto it. Two glass tubes were sealed

(11) Roth, W. A., and Becker, G., Z. physik. Chem., A159, 27 (1932).

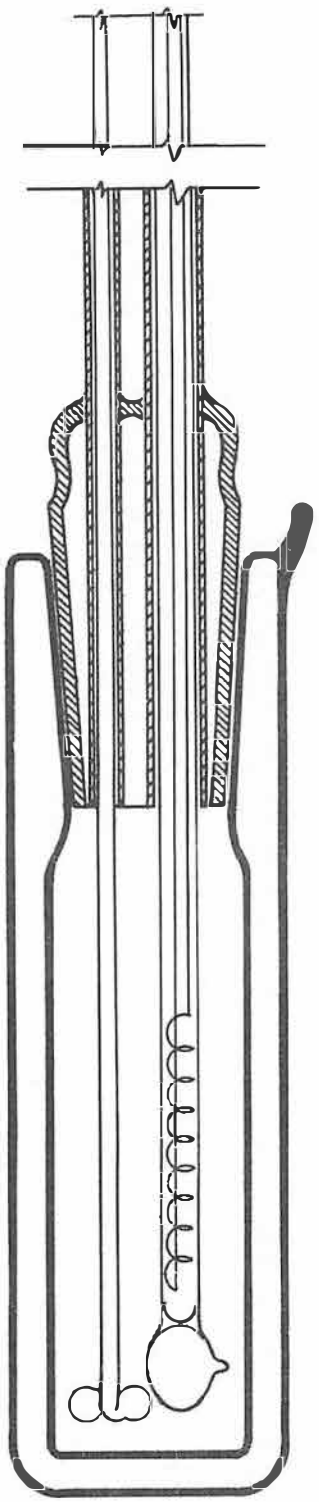


FIGURE 11.- SOLUTION CALORIMETER

vertically into the top which provided inlets for the platinum resistance thermometer and the glass stirrer used to stir the contents of the calorimeter. The calorimeter was submerged in a thermostat bath controlled to ± 0.002°.

About 100 - 200 mg. of technetium heptoxide was sealed in a small thin-walled glass bulb which was cemented to the end of the platinum resistance thermometer. The bulb could then be broken by applying a slight pressure on the top of the thermometer. The stirrer was rotated at 250 r.p.m. by a synchronous motor. The calorimeter contained 32.0 ml. of water which served as both solvent and as a calorimeter medium. The resistance of the platinum resistance thermometer was measured as before, except that the individual measurements were determined to ± 0.0001 ohms, or ± 0.001°. The temperature rise was about 0.3°, so that this still gave a precision of about 0.3 percent. The total temperature rise was measured by taking the rise at the 0.6 time as in the combustion calorimetry.

The calorimeter was calibrated by the neutralization of an aqueous sodium hydroxide solution with a slight excess of hydrochloric acid to form water. The sodium hydroxide solution was weighed into a small glass bulb and broken in the hydrochloric acid solution. The heat data for sodium hydroxide, sodium chloride and hydrochloric acid were taken from Harned and Owen.[12] Corrections were made for the

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(12) Harned, H. S., and Owen, B. B., "The Physical Chemistry of Electrolytic Solutions", Reinhold Publishing Co., New York, N. Y., 1943, p. 541.

heats of dilution. During the measurements Calorimeter I was accidentally broken and a second one had to be constructed. The agreement (see Table XIV) between values obtained from the two calorimeters was therefore gratifying.

From the calibration data of Table XIII, and the heat data from Table XIV, the heat of solution at 25° of the oxide was estimated:

$$H_2O_{(l)} + Tc_2O_{7(s)} + aq. = 2HTcO_4(0.04\ \underline{M}.) \qquad \triangle H = -11.59 \pm 0.08 \text{ kcal.} \qquad \text{(IV-6)}$$

Since this solution is so dilute, we shall assume that this heat also represents the heat of solution of the oxide to give an infinitely dilute solution.

C. The Heat of Dilution of a Pertechnic Acid Solution

Since the solution of pertechnic acid formed in the combustion bomb experiments was still relatively concentrated, it was necessary to determine the heat of dilution of this solution to essentially infinite dilution, to see if an appreciable amount of heat were involved. The heat of solution calorimeter previously described was used. Two ml. of a 0.328 M. pertechnic acid solution was sealed in a small glass bulb and broken in the calorimeter containing 30.00 ml. of water to give a solution which was 0.0205 M. The heat change of -0.005° corresponded to the absorption of 0.28 kcal. mole^{-1} of acid. As before, it was assumed that this latter concentration of pertechnic acid is essentially infinitely dilute.

TABLE XIII

CALIBRATION OF SOLUTION CALORIMETER

Calorimeter	Loading[a]	M.e. H_2O Formed	$\triangle H$[b]	$\triangle T$	$\bar{C}$[c]	$\bar{C}_{corr.}$[d]
I	32.00	0.994	-12,981	0.2037°	39.7_7	39.7_7
I	31.97	0.971	-12,981	0.3184	39.5_7	39.6_0
				Average:		$39.6_9 \pm .09$
II	31.86	0.862	-13,000	0.2833	38.9_2	38.8_2

[a]Grams of H_2O.

[b]Corrected for heats of dilution of NaOH, HCl, NaCl.

[c]In cal. deg.$^{-1}$ at 25°.

[d]Adjusted to loading of 32.00 ml. at 25°.

TABLE XIV

HEAT OF SOLUTION OF TECHNETIUM HEPTOXIDE

Calorimeter	Wt. Tc_2O_7	$\triangle T$	Conc.[a]	$-\blacktriangle H$ soln.[b]
I	215.6 mg.	0.2045°	0.0448	11.67
II	182.0	0.1741	0.0368	11.51
		Average:	0.0408	11.59 ± 0.08

[a]Concentration of resulting solution in moles $l.^{-1}$.

[b]In kcal. $mole^{-1}$ of Tc_2O_7.

The heat of combustion of technetium to give anhydrous technetium heptoxide and pertechnic acid at infinite dilution ($HTcO_{4(aq)}$) can now be calculated.

From equation (IV-5):

$$2Tc(s) + 7/2\ O_{2(g)} + H_2O_{(l)} + aq. = 2HTcO_4(0.3\ \underline{M.}) \qquad (IV\text{-}5)$$
$$\triangle H = -278.3 \pm 2.8 \text{ kcal.}$$

Adding to this

$$2HTcO_4(0.3\ \underline{M.}) + aq. = 2HTcO_{4(aq.)} \qquad (IV\text{-}7)$$
$$\triangle H = +0.6 \text{ kcal.}$$

$$2Tc(s) + 7/2\ O_{2(g)} + H_2O_{(l)} + aq. = 2HTcO_{4(aq.)} \qquad (IV\text{-}8)$$
$$\triangle H = -277.7 \pm 2.8 \text{ kcal.}$$

is obtained. Adding

$$2HTcO_{4(aq.)} = Tc_2O_{7(s)} + H_2O_{(l)} + aq. \qquad (IV\text{-}6)$$
$$\triangle H = 11.6 \pm 0.1 \text{ Kcal.}$$

to (IV-8) gives:

$$2Tc(s) + 7/2\ O_{2(g)} = Tc_2O_{7(s)} \qquad (IV\text{-}9)$$
$$\triangle H = -266.1 \pm 2.6 \text{ kcal.}$$

Taking the value of 68,317.1 cal.mole^{-1} for the heat of formation of water[13] under standard conditions at 25° and adding it to equation

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(13) "Selected Values of Chemical Thermodynamic Properties", National Bureau of Standards, Washington, D. C., 1948, Series I.

(IV-8), the heat of formation of aqueous pertechnic acid from its elements is:

$$Tc(s) + 2\ O_{2(g.)} + \tfrac{1}{2}\ H_{2(g.)} + aq. = HTcO_{4(aq.)} \qquad \text{(IV-10)}$$

$$\triangle H = -173.0 \pm 1.7 \text{ kcal.}$$

CHAPTER V

OXIDATION REDUCTION CELLS

Both manganese and rhenium form dioxides which can be used to study the oxidation potential of the element from the +4 to the +7 oxidation state. These compounds form reversible electrodes; the manganese dioxide-permanganate electrode has been discussed by Walkley,[1] and Hugus[2] has recently measured the rhenium dioxide-perrhenate potential.

The oxidation potential for the technetium dioxide-pertechnetate electrode has been measured in both acid and basic solutions for the thermodynamic characterization of technetium dioxide. Both types of cells were used to prove that the electrodes are reversible and that the electrode equations are as follows:

$$\text{(acid)} \qquad TcO_2 + 2H_2O = TcO_4^- + 4H^+ + 3e^- \qquad \text{(V-1)}$$

$$\text{(base)} \qquad TcO_2 + 4OH^- = TcO_4^- + 2H_2O + 3e^- \qquad \text{(V-2)}$$

With the measured potential of the basic cell, the voltage of the acid cell can be calculated and compared with the measured value. Good agreement was obtained for these cells.

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(1) Wadsley, A. D., and Walkley, H., J. Electrochem. Soc., 95, 11 (1949).

(2) Hugus, Z., and Latimer, W. M., To appear in the new edition of "Oxidation Potentials", 1952.

A. Acid Cell

The half-cell consisted of a test tube about 3 in. long and 1 in. in diameter, fitted with a rubber stopper. Inserted through the stopper was a platinum rod with a small cup on its end to contain the technetium dioxide. A glass stirrer extending into the cell was rotated slowly during the measurements to avoid polarization of the electrode. The cell solution of pertechnic acid was made by dilution of a more concentrated, standardized solution. This concentration was also rechecked after each determination by converting the solution to ammonium pertechnetate and weighing. The half-cell was connected by a salt-bridge of 1.8 M. potassium nitrate and 1.8 M. potassium chloride solution as recommended by Grove-Rasmussen[3] to a silver-silver chloride half-cell of known voltage. The two half-cells were immersed in a thermostat at 25°. The voltage of the cell was measured on a type K-2 Leeds and Northrup potentiometer, which was standardized before each reading against a standard Eppley cell, calibrated by the National Bureau of Standards.

The salt-bridge was constructed of pyrex tubing in the form of an inverted U-tube, the two ends of which contained sealed-in fibers, obtained from two commercial calomel electrodes. These fibers provided solution contact between the two half-cells, but prevented diffusion of any but trace amounts of bridge solution into either half-cell compartment.

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(3) Grove-Rasmussen, K. V., Acta. Chem. Scand., 5, 422 (1951).

The technetium dioxide used in one series of determinations was prepared by Nelson[4] by the reduction of aqueous ammonium pertechnetate solution with zinc and hydrochloric acid. For the second series of experiments, an electrode of platinum gauze was used onto which black deposits of technetium dioxide had been electroplated from ammonium pertechnetate solutions. These deposits were not characterized by chemical means, although rhenium dioxide prepared in this manner is well known.[5] Since the voltage of this electrode was the same within experimental error as the voltage of the other technetium dioxide electrode, it was concluded that such a procedure does result in technetium dioxide.

The silver-silver chloride half-cell was made from a silver wire which had been cleaned in nitric acid and thoroughly washed. It was used as the anode in an electrolytic cell containing dilute hydrochloric acid. Brief electrolysis in this cell formed a thin adherent deposit of silver chloride on the silver wire. After washing, this electrode was immersed in a hydrochloric acid solution of known concentration. The cell can be represented as:

$$Ag/AgCl : HCl :: \begin{matrix} KNO_3 \\ KCl \end{matrix} :: HTcO_4 : TcO_2/Pt \qquad (V\text{-}3)$$

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(4) Nelson, C. M., "The Magnetochemistry of Technetium and Rhenium", Doctoral Dissertation, The University of Tennessee, 1952; the author is indebted to Dr. Nelson for the use of this compound.

(5) Druce, J. G. F., "Rhenium", The University Press, Cambridge, England, 1948, p. 32.

The data for the cell at various acid concentrations are given in Table XV. The reaction for the entire cell can be written:

$$3Ag + 3HCl + HTcO_4 = 3AgCl + 2H_2O + TcO_2 \qquad (V\text{-}4)$$

for which:

$$E = E^o + \frac{0.0591}{n} \log a^3_{HCl}\, a_{HTcO_4} \qquad (V\text{-}5)$$

where n refers to the number of electrons (3) involved in the oxidation and the a's refer to activities of HCl and $HTcO_4$. Since the HCl concentration was kept constant (0.05 M.), the product of the activity coefficient,[6] 0.8304, times the concentration, 0.05, can be substituted for the activity of the HCl. This quantity must then be squared, since the activities referred to in equation (V-5) are mean ionic activities. Substituting numerical values:

$$E = E^o - 0.1634 + 0.0394 \log m_{HTcO_4} + 0.0394 \log \gamma_{HTcO_4} \qquad (V\text{-}6)$$

In this equation the activity of pertechnic acid has been replaced by the appropriate molalities and activity coefficients. If it is further assumed that the activity coefficient of the pertechnic acid in very dilute solutions can be considered as:[7]

$$\log \gamma_{HTcO_4} = -0.5065\ M.^{\frac{1}{2}} \qquad (V\text{-}7)$$

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(6) Harned, H. S., and Owen, B. B., "The Physical Chemistry of Electrolytic Solutions", Reinhold Publishing Company, New York, N. Y., 1943, p. 547.

(7) Harned, H. S., and Owen, B. B., ibid., p. 119.

TABLE XV

EMF OF THE TECHNETIUM DIOXIDE-PERTECHNETATE ELECTRODE IN PERTECHNIC ACID SOLUTIONS

Electrode (+)	$E_{obs.}$	$\underline{M.}$[a]	$-\log \underline{M.}$	$-0.0394 \log \underline{M.}$	E_1[b]
TcO_2 (from	0.276	0.00135	2.870	0.1131	0.552
zinc re-	0.269	0.000679	3.168	0.1248	0.557
duction)	0.251	0.000338	3.471	0.1380	0.552
	0.231	0.000135	3.870	0.1520	0.546
				average:	0.552 ± 0.003
TcO_2	0.268	0.00179	2.747	0.1082	0.540
(electro-	0.256	0.000897	3.047	0.1201	0.549
lytic)				average:	0.545 ± 0.005
				Total average:	0.549 ± 0.004 volts

[a] In moles $l.^{-1}$ of pertechnic acid.

[b] $E_1 \equiv E_{obs.} - 0.0394 \log \underline{M.} + 0.1634$ volts, against the Ag–AgCl electrode.

the expression for the cell voltage as a function of concentration then becomes:

$$E = E^{o} - 0.1634 + 0.0394 \log \underline{M.}_{HTcO_4} - 0.01997 \underline{M.}^{\frac{1}{2}} \qquad (V\text{-}8)$$

or, on rearranging,

$$E_1 \equiv E + 0.1634 - 0.0394 \log \underline{M.}_{HTcO_4} = E^{o} - 0.01997 \underline{M.}^{\frac{1}{2}} \qquad (V\text{-}9)$$

When the left side of equation (V-9) is plotted against the square root of the concentration, a straight line of almost zero slope, and an intercept at zero concentration equal to E^{o} for cell reaction (V-4), is obtained.

The cell reaction indicates that the technetium dioxide electrode should be the positive electrode, and this was also verified.

Calculations using equation (V-9) are given in Table XV. At concentrations above .00135 M. some deviation from the limiting behavior was noticed; hence, only the lower concentrations are considered. Part of this deviation may be due to the unknown effect of the junction potentials on the cell voltages.

The average value of the defined E_1 above will be equal to E^{o} since the last term in equation (V-9) is negligible at the concentrations given in Table XV. From Table XV, E_1 is equal to 0.549 ± 0.004 volts. E^{o} for the total cell reaction is the sum:

$$E^{o} = E^{o}_{TcO_2\text{-}TcO_4^-} + E^{o}_{Ag\text{-}AgCl} \qquad (V\text{-}10)$$

Using the value for E^o of the Ag-AgCl electrode as -0.222 volts[8], the voltage for the half-cell reaction (V-1) becomes -0.771 volts. These values are, of course, based on the usual assumptions that the voltage of the hydrogen electrode at unit activity is zero, and that the junction potential is negligible at these low concentrations.

B. Basic Cell

The basic cell was constructed in the same manner as the acid cell, except that the dioxide-pertechnetate half-cell contained sodium pertechnetate and sodium hydroxide of equal concentrations. These were formed *in situ* by pipetting the required amounts of standardized pertechnic acid and sodium hydroxide solutions into a known amount of distilled water already in the cell compartment. The reference electrode in this case was the mercury-mercuric oxide electrode in a sodium hydroxide solution. The cell was first constructed with the two electrodes immersed in the same solution, but this method was abandoned because of the tendency for the finely-divided technetium oxide to become mixed in with the mercuric oxide of the other electrode. Therefore, the half cells were separated, using the same salt bridge as for the acid cell.

The technetium dioxide electrode used first was of the same type as used in the acid cell. However, difficulty was experienced in getting the technetium dioxide to stay in the cup, since it apparently disinte-

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(8) Harned, H. S., and Ehlers, R. W., J. Am. Chem. Soc., 54, 1350 (1932).

grates in basic solution into very fine particles. Hence, the voltage of the cell was not steady, and this electrode was unsatisfactory. The electrode which finally gave satisfactory results was obtained by plating technetium dioxide onto a platinum gauze as in the case of the acid cell. The technetium dioxide so formed is very adherent, and serves as a satisfactory electrode from a physical standpoint.

The two half-cells were immersed in a thermostat at 25°, and the voltages read as before. Some difficulty was experienced in that the voltage of the cell drifted with time. This was possibly due to carbon dioxide absorption by the basic solution with a subsequent change in the hydroxyl ion concentration. However, when nitrogen gas was passed through the cell to avoid this difficulty, the voltage still drifted (fell). It had also been observed previously in the acid cell that when nitrogen gas was bubbled through the solution, the normally stable voltages fell. This could be due to the nitrogen undergoing some catalytic reaction at the technetium dioxide electrode, or to an electrode poison in the gas. Since the drift was not very rapid, the data recorded in Table XVI for this cell were taken during the first few hours.

Below a concentration of about 0.06 M. TcO_4^-, the cell voltage was neither steady nor reproducible. The same effect has been observed for the basic ReO_2-ReO_4^- electrode.[9] Since the technetium was not available for more concentrated solutions, it was not possible

(9) Hugus, Z., and Latimer, W. M., University of California Radiation Laboratory Chemistry Division Quarterly Report, UCRL-1196, 1951.

to make a concentration study. However, it will be shown that this is not necessary in the case of the basic cell, because of the form of the cell reaction. Two different electrodes were used, however, to obtain the data reported in Table XVI.

The cell may be represented as:

$$Hg/HgO : NaOH :: \frac{KCl}{KNO_3} :: \frac{NaTcO_4}{NaOH} : TcO_2/Pt \qquad (V\text{-}11)$$

The cell reaction may be written:

$$2NaTcO_4 + 3Hg + H_2O = 3HgO + 2TcO_2 + 2NaOH \qquad (V\text{-}12)$$

and the expression for the voltage is:

$$E_B = E_B^o - \frac{.0591}{3} \log \frac{a^2_{NaOH}}{a^2_{NaTcO_4}} \qquad (V\text{-}13)$$

Since the concentrations of sodium hydroxide and sodium pertechnetate were the same, then:

$$E_B = E_B^o - \frac{(2)(.0591)}{3} \log \frac{\gamma_{NaOH}}{\gamma_{NaTcO_4}} \qquad (V\text{-}14)$$

It can be seen that in dilute solutions, where the activity coefficients of all 1:1 electrolytes are about the same, the measured voltage should correspond to the E_B^o for the cell reaction, (V-12). The cell reaction requires the technetium dioxide electrode in this case to be the negative electrode (anode), which was verified.

Using the average value of 0.409 ± 0.004 volts (see Table XVI) for the cell reaction and subtracting 0.098 volts for the mercury-

TABLE XVI

EMF OF THE TECHNETIUM DIOXIDE-PERTECHNETATE ELECTRODE IN BASIC SOLUTION

TcO_2 Electrode[a],(-)	Concentration	Voltage[b]
I	0.0683 M. $NaTcO_4$ 0.0683 M. NaOH	0.413 ± 0.003
II	0.0683 M. $NaTcO_4$ 0.0683 M. NaOH	0.406 ± 0.005
	Average:	0.409 ± 0.004 volts

[a]Electrolytic deposit on platinum.

[b]Against the Hg/HgO-electrode.

mercuric oxide electrode[10] the voltage for half cell reaction (V-2) becomes 0.311 volts:

$$TcO_2 + 4OH^- = TcO_4^- + 2H_2O + 3e^- \qquad (V\text{-}2)$$

$$E_B^o = +0.311 \pm 0.004 \text{ volts}$$

The two cells now can be compared as a test of the assumptions involved in calculating the E^o for the acid and basic cells. To convert from the basic to acid cell voltages:

$$\triangle E = E_B^o - E_A^o = \frac{0.0591}{3} \log \frac{(H^+(\text{unit activity}))^4}{(H^+(\text{in 1 } \underline{M.} \ O\overline{H} = 10^{-14} \ \underline{M.}))^4} \qquad (V\text{-}15)$$

$$\triangle E = E_B^o - E_A^o = +1.103 \text{ volts} \qquad (V\text{-}16)$$

Therefore $E^o_{B(calc.)} = 1.103 - 0.771 = +0.332$ volts. The mean average for both of these cells will be taken as:

$$\overline{E}_A^o = -0.782 \pm 0.011 \text{ volts} \qquad (V\text{-}17)$$

$$\overline{E}_B^o = 0.322 \pm 0.011 \text{ volts} \qquad (V\text{-}18)$$

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(10) MacInnes, D. A., "The Principles of Electrochemistry", Reinhold Publishing Company, New York, N. Y., 1939, p. 254.

CHAPTER VI

THERMOCHEMICAL CALCULATIONS

The heats and free energies of formation and reactions involving a number of compounds of technetium can now be calculated from the data given in the previous chapters taken together with the entropy values for technetium and its compounds given in Appendix V. From the free energies of formation of the oxides, the bond energy of the technetium-oxygen bond can be estimated. These values will then be compared to the available data on other elements of Group VII in an attempt to show, once again, that the periodic arrangement of elements is useful in predicting the properties of a new element. All of the auxiliary data, unless otherwise specified, have been obtained from two sources: absolute entropies from the compilation of Kelley[1], and heats and free energies of formation from the Bureau of Standards Tables.[2] While the thermodynamic data are given to five significant figures, this is intended for calculational purposes only. The uncertainties in values are given in Table XVIII and for the most part amount to about 1-2 percent.

A. The Free Energies, Heats, and Entropies of Formation of Technetium (VII) Compounds

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(1) Kelley, K. K., U. S. Bur. Mines Bull., 477, 1950.

(2) "Selected Values of Chemical Thermodynamic Properties", U. S. Bureau of Standards, Washington, D. C., 1948, Series I, II, III.

From the heat of formation of solid technetium heptoxide (Chapter IV) of -266,100 cal. mole^{-1}, and the entropy of technetium heptoxide (Appendix V) of 39.0 e.u., the entropy of formation, and thus, the free energy of formation of the heptoxide can be calculated to be -222,540 cal. mole^{-1}:

$$2Tc_{(s)} + 7/2\ O_{2(g.)} = Tc_2O_{7(s)}$$
$$\triangle H^o = -266,100 \text{ cal.}$$
$$\triangle F^o = -222,540 \qquad \text{(VI-1)}$$
$$\triangle S^o = -146.1 \text{ e.u.}$$

Using the vapor pressure data (Chapter III) for the heptoxide, the thermodynamic functions for the heptoxide vapor become:

$$2Tc_{(s)} + 7/2\ O_{2(g.)} = Tc_2O_{7(v)}$$
$$\triangle H^o = -233,150 \text{ cal.}$$
$$\triangle F^o = -210,580 \text{ cal.} \qquad \text{(VI-2)}$$
$$\triangle S^o = -75.7 \text{ e.u.}$$

From the entropy of formation of the vapor, and the absolute entropies of oxygen and technetium, the entropy of the heptoxide vapor at 25° is 109.4 e.u. This value indicates that the gaseous technetium heptoxide molecule must have a considerable number of rotational and vibrational degrees of freedom.

The heat of formation of pertechnic acid can be calculated from the vapor pressure data of Chapter III and equation (VI-1). Using $\triangle H$ as 430 cal., $\triangle F$ as 1632 cal., and $\triangle S$ as -4.0 e.u., for the decomposition

into the heptoxide and water, the following is obtained:

$$2Tc_{(s)} + 7/2\ O_{2(g)} + H_2O_{(l)} = 2HTcO_4(s)$$
$$\Delta H = -266{,}530 \text{ cal.}$$
$$\Delta F = -224{,}171 \text{ cal.} \qquad \text{(VI-3)}$$
$$\Delta S = -142.1 \text{ e.u.}$$

from which it follows:

$$Tc_{(s)} + \tfrac{1}{2}\ H_{2(g)} + 2\ O_{2(g)} = HTcO_4(s)$$
$$\Delta H^o = -167{,}420 \text{ cal.}$$
$$\Delta F^o = -140{,}430 \text{ cal.} \qquad \text{(VI-4)}$$
$$\Delta S^o = -90.5 \text{ e.u.}$$

For solutions of pertechnic acid the following quantities were calculated from (IV-4), vapor pressure measurements (Chapter III), heats of solution (Chapter IV), and entropies (Appendix V):

$$Tc_{(s)} + \tfrac{1}{2}\ H_{2(g)} + 2\ O_{2(g)} + aq. = HTcO_4(0.3\ \underline{M}.) \qquad \text{(VI-5)}$$
$$\Delta H^o = -173{,}300 \text{ cal.}$$

$$Tc_{(s)} + \tfrac{1}{2}\ H_{2(g)} + 2\ O_{2(g)} + aq. = HTcO_4(sat.)$$
$$\Delta H^o = -167{,}760 \text{ cal.} \qquad \text{(VI-6)}$$
$$\Delta F^o = -141{,}980 \text{ cal.}$$
$$\Delta S^o = -86.4 \text{ e.u.}$$

and

$$Tc_{(s)} + 2\ O_{2(g)} + \tfrac{1}{2}\ H_{2(g)} + aq. = HTcO_4\ (aq.)$$
$$\Delta H^o = -173{,}000 \text{ cal.}$$
$$\Delta F^o = -150{,}550 \text{ cal.} \qquad \text{(IV-10)}$$
$$\Delta S^o = -75.3 \text{ e.u.}$$

The cell potential of the hypothetical half-cell reaction involving technetium metal and pertechnetate ion can now be calculated:

$$Tc_{(s)} + 4H_2O + aq. = TcO_4^-{}_{(aq.)} + 8H^+ + 7e^- \qquad (VI\text{-}7)$$

$$\Delta F = \Delta F^o_{f(TcO_4^-,aq.)} - 4\Delta F^o_{f(H_2O)} = 76{,}211 \text{ cal.}$$

$$E^o = -\Delta F/23{,}061(7) = -0.472 \text{ volts}$$

The potential of the technetium-technetium dioxide couple then becomes -0.240 volts from equations (VI-7) and (V-17).

The heat and free energy of formation of potassium pertechnetate can be calculated from the solubility data of Parker[3] and the data already recorded in (VI-1 through VI-6). Parker gives the $K_{s.p.}$ for potassium pertechnetate as 0.44 at 27° and 0.14 at 7°. From the equation:

$$\log \frac{K_{s.p.(1)}}{K_{s.p.(2)}} = \frac{-\Delta H}{2.303\ R}\,(1/T_1 - 1/T_2) \qquad (VI\text{-}8)$$

the heat of solution is calculated to be 9,550 cal. $mole^{-1}$. If we further neglect the heat of dilution of a saturated solution to infinite dilution, then:

$$KTcO_4(s) + aq. = KTcO_4(aq.) \qquad (VI\text{-}9)$$

$$\Delta H = 9{,}550 \text{ cal.}$$

$$\Delta F^o = 490 \text{ cal.}$$

$$\Delta S^o = 30.2 \text{ e.u.}$$

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(3) Parker, G. W., Oak Ridge National Laboratory Chemistry Division Quarterly Report, ORNL-1116, 1951.

where the free energy of solution was calculated from:

$$\Delta F^{o} = -2.303\ RT \log K_{s.p.} \qquad \text{(VI-10)}$$

No correction for the temperature difference between 25° and 27° has been made.

It was shown in Chapter II that pertechnic acid behaved like a strong acid. Assuming therefore, that its heat of neutralization by potassium hydroxide at infinite dilution is -13,308 calories, the heat of formation of solid potassium pertechnetate may be calculated:

$$K_{(s)} + Tc_{(s)} + 2\ O_{2(g)} = KTcO_4(s)$$

$$\Delta H^{o} = -237{,}830 \text{ cal.}$$

$$\Delta F^{o} = -213{,}710 \text{ cal.} \qquad \text{(VI-11)}$$

$$\Delta S^{o} = -80.9 \text{ e.u.}$$

The details of this calculation are given in Table XVII.

The entropy of technetium heptoxide deserves special attention. The entropies of most of the lower oxides of technetium can be estimated fairly accurately, as was done in Appendix V, by comparing the contribution of the oxygen in similar oxides and using Latimer's tables[4] for the contribution of the metal atom. However, there is so little information on the higher oxides, that this method is subject to more uncertainty. In addition, the large entropy of fusion of technetium heptoxide indicates that some of the contributions of rotation and

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(4) Latimer, W. M., J. Am. Chem. Soc., 73, 1480 (1951).

TABLE XVII

THE HEAT OF FORMATION OF POTASSIUM PERTECHNETATE

Reaction	$-\triangle H$
(1) $2K_{(s)} + 2H_2O_{(l)} + aq. = 2KOH_{(aq.)} + H_{2(g)}$	93,366 cal.
(2) $2Tc_{(s)} + 7/2\ O_{2(g)} + H_2O_{(l)} + aq. = 2HTcO_4(aq.)$	277,700
(3) $2KOH_{(aq.)} + 2HTcO_4(aq.) = 2KTcO_4(aq.) + 2H_2O_{(l)}$	26,616
(4) $2KTcO_4(aq.) = 2KTcO_4(s) + aq.$	19,200[a]
(5) $H_{2(g)} + \frac{1}{2}\ O_{2(g)} = H_2O_{(l)}$	68,317
$2K_{(s)} + 2Tc_{(s)} + 4\ O_{2(g)} = 2KTcO_4(s)$	485,199
or $\triangle H_f^o = -242{,}600$ cal. mole^{-1}	

[a]From solubility data of Parker (Parker, G. W., Oak Ridge National Laboratory Chemistry Division Quarterly Report, ORNL-1116, 1951) and assuming the heat of dilution of the saturated solution is negligible.

vibration present in normal crystalline solids may be peculiarly lacking in solid technetium heptoxide and consequently estimates of this nature would not be justified. From what data exists, however, the entropy calculated by the same method as the other oxides is 43.9 e.u. Another method which can be applied is to base the entropy upon that for solid pertechnic acid and the entropy change for:

$$\tfrac{1}{2}Tc_2O_7(s) + \tfrac{1}{2}H_2O(l) = HTcO_4(s) \qquad \Delta S = 2.0 \text{ e.u.} \qquad \text{(VI-12)}$$

from Table IX. With an entropy of 29.9 e.u. for $HTcO_4(s)$, the calculated entropy of $Tc_2O_7(s)$ is 39.0 e.u. at 25°. The latter value is adopted because the entropy calculated from the additivity of the oxides is so uncertain.

B. The Free Energy, Heat, and Entropy of Formation of Technetium Dioxide

The free energy, enthalpy, and entropy of formation of technetium dioxide can be calculated from the cell voltages given in Chapter V:

$$TcO_2(s) + 2H_2O(l) + aq. = TcO_4^-(aq.) + 4H^+ + 3e^- \qquad \text{(V-1,17)}$$

$$E^o = -0.782 \text{ volts}$$

$$\Delta F^o = 54{,}101 \text{ cal.}$$

The free energy of formation of TcO_2 is then:

$$\Delta F_f^\circ = \Delta F_{f(TcO_4^-,\ aq.)}^\circ - 2\Delta F_{f(H_2O)}^\circ - 54{,}101 = -91{,}270 \text{ cal. mole}^{-1} \qquad \text{(VI-13)}$$

Using the value of 14.9 e.u. for the entropy of technetium dioxide, the entropy of formation becomes -40.9 e.u., and the heat of formation at 25° is -103,465 cal. $mole^{-1}$:

$$\begin{aligned} Tc_{(s)} + O_{2(g)} &= TcO_{2(s)} \\ \Delta H^\circ &= -103{,}460 \text{ cal.} \\ \Delta F^\circ &= -91{,}270 \text{ cal.} \\ \Delta S^\circ &= -40.9 \text{ e.u.} \end{aligned} \qquad \text{(VI-14)}$$

C. The Free Energy, Heat, and Entropy of Formation of Technetium Trioxide

Although none of the thermodynamic properties of technetium trioxide has been measured directly, the heat of formation of this compound can, nevertheless, be estimated with fair accuracy. The method may be based on the assumption that the difference between the heats of formation of technetium trioxide and technetium heptoxide is the same as the difference between the heats of formation of rhenium trioxide and rhenium heptoxide. This difference is 3 kcal. $mole^{-1}$ ReO_3 (See A IV-5). The estimated heat of formation for technetium trioxide then becomes:

$$\begin{aligned} \Delta H_f^\circ &= \tfrac{1}{2}\Delta H_{f(Tc_2O_7)}^\circ - 3.0 \\ \Delta H_f^\circ &= -130 \pm 3 \text{ kcal. mole}^{-1} \end{aligned} \qquad \text{(VI-15)}$$

An estimation can also be based on the fact that technetium trioxide has been observed to disproportionate in water (Chapter II):

$$3TcO_3(s) + H_2O_{(l)} + aq. = 2HTcO_{4(aq.)} + TcO_2(s) \qquad (II\text{-}5,6)$$
$$\Delta F \leq 0$$

The value of the free energy of formation which causes the free energy change for this reaction to be slightly negative (by 2-3 kilocal.) is -109,740 cal. mole^{-1} of technetium trioxide. Using 15.7 e.u. for the entropy of technetium trioxide, the heat of formation which will enable reaction (II-5,6) to be spontaneous is -129,000 ± 5000 cal. mole^{-1}. Since this value is within the experimental error given in (VI-15), it is adopted for the heat of formation:

$$Tc_{(s)} + 3/2\ O_{2(g)} = TcO_3(s) \qquad (VI\text{-}16)$$
$$\Delta H^o = -129{,}000 \text{ cal.}$$
$$\Delta F^o = -109{,}740 \text{ cal.}$$
$$\Delta S^o = -64.6 \text{ e. u.}$$

The half-cell reactions for the trioxide-pertechnetate and the trioxide-dioxide couples can be calculated from the free energy of formation of technetium trioxide. These cell reactions are, of course, hypothetical since the trioxide reacts with water; however, such voltages are of interest in estimating the strength of an oxidation-reduction system.

For the technetium trioxide-pertechnetate electrode:

$$TcO_{3(s)} + H_2O_{(l)} + aq. = TcO_{4(aq.)}^{-} + 2H^{+} + e^{-}$$

$$\Delta F^{o} = \Delta F^{o}_{f(TcO_4^-,aq.)} - \Delta F^{o}_{f(TcO_3)} - \Delta F^{o}_{f(H_2O)} \qquad \text{(VI-17)}$$

$$\Delta F^{o} = 14{,}880 \text{ cal.}$$

$$E^{o} = -14{,}880/23{,}061 = -0.65 \text{ volts}$$

and for the technetium dioxide-trioxide couple:

$$TcO_{3(s)} + 2H^{+} + 2e^{-} = TcO_{2(s)} + H_2O_{(l)}$$

$$\Delta F^{o} = \Delta F^{o}_{f(TcO_2)} + \Delta F^{o}_{f(H_2O)} - \Delta F^{o}_{f(TcO_3)} \qquad \text{(VI-18)}$$

$$\Delta F^{o} = -38{,}220 \text{ cal.}$$

$$E^{o} = 38{,}220/2 \times 23{,}061 = 0.83 \text{ volts}$$

Because of the instability of technetium trioxide in aqueous solutions, neither the reduction of pertechnetate ion nor the oxidation of technetium dioxide to the trioxide is feasible. The voltages indicate that such oxidations and reductions might well be carried out in non-aqueous media. The free energies also indicate why technetium heptoxide is so easily decomposed by organic materials:

$$Tc_2O_{7(s)} + CO_{(g)} = 2TcO_{3(s)} + CO_{2(g)} \qquad \text{(VI-19)}$$

$$\Delta F^{o} = -58.4 \text{ kcal.}$$

and also:

$$TcO_{3(s)} + CO_{(g)} = TcO_{2(s)} + CO_{2(g)} \qquad \text{(VI-20)}$$

$$\Delta F^{o} = -43.0 \text{ kcal.}$$

Consequently, the oxidation of TcO_2 by carbon dioxide to higher oxides is not feasible.

D. The Oxidation-Reduction Scheme for Technetium

The oxidation-reduction scheme for technetium, technetium dioxide, technetium trioxide, and pertechnetate can be constructed following the method used by Latimer.[5] Such a diagram may be used to determine the likelihood of a given reaction occurring in aqueous media. Potential diagrams are given for both unit activity hydrogen and hydroxyl ion. Voltages in basic solutions can be calculated from the acid potentials by reason of the fact that the hydrogen ion concentration is 10^{-14} M. in a basic solution of unit activity. The potential diagram for technetium is given in Figure 12. The value for the Tc^{-1} potential is estimated from the value of 0.4 volt for the Re^{-1} potential estimated by Latimer.[6]

A summary of the calculated and measured thermodynamic properties of technetium and its compounds is given in Table XVIII.

E. Comparison of the Properties of Sub-group VII

A comparison of the thermodynamic properties of the other members of sub-group VII, manganese and rhenium, indicates that in general the properties of technetium are intermediate between

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(5) Latimer, W. M., "Oxidation Potentials", Prentice-Hall, New York, N.Y., 1938.

(6) Latimer, W. M., loc. cit., p. 227.

TABLE XVIII

SUMMARY OF THERMODYNAMIC PROPERTIES OF TECHNETIUM AND ITS COMPOUNDS
(25°)

Compound	$-\Delta H_f^\circ$	$-\Delta F_f^\circ$	$-\Delta S_f^\circ$	$S^{o(b)}$
$Tc_{(s)}$	0 cal.	0 cal.	0 e.u.	6.8 ± 0.2 e.u.
$Tc_{(g)}$	---	---	-36.5 ± 0.2	43.26 ± 0.01
$TcO_{2(s)}$	103,460 ± 2000[a]	90,270 ± 2000	+40.9 ± 0.5	14.9 ± 0.5
$TcO_{3(s)}$	129,000 ± 5000	109,740 ± 5000	64.6 ± 0.6	15.7 ± 0.6
$Tc_2O_{7(s)}$	266,100 ± 2600	222,540 ± 2600	146.1 ± 2.0	39.0 ± 2.0
$Tc_2O_{7(l)}$	249,500 ± 2600	218,500 ± 2600	104.0 ± 2.0	81.1 ± 2.0
$Tc_2O_{7(v)}$	233,150 ± 2600	210,580 ± 2600	75.7 ± 2.0	109.4 ± 2.0
$HTcO_{4(s)}$	167,420 ± 1300	140,430 ± 1300	90.5 ± 2.0	29.9 ± 2.0
$HTcO_{4(sat.)}$	167,760 ± 1300	141,980 ± 1300	86.4 ± 2.0	
$HTcO_{4}$(0.3 M.)	173,300 ± 1300	---	---	---

TABLE XVIII

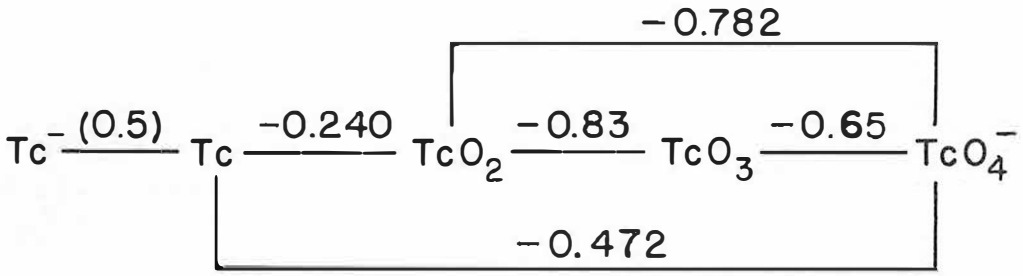
SUMMARY OF THERMODYNAMIC PROPERTIES OF TECHNETIUM AND ITS COMPOUNDS (Continued)
(25°)

Compound	$-\triangle H_f^o$	$-\triangle F_f^o$	$-\triangle S_f^o$	$S^{o(b)}$
$TcO_4^-(aq.)$	173,000 ± 1300	150,550 ± 1300	75.3 ± 1.0	45.1 ± 1.0
$KTcO_4(s)$	242,600 ± 1500	216,480 ± 1500	80.9 ± 1.0	39.1 ± 1.0
$NaTcO_4(s)$	---	---	79.6 ± 1.0	37.4 ± 1.0
$NH_4TcO_4(s)$	---	---	146.3 ± 1.0	43.8 ± 1.0
$K_2TcCl_6(s)$	---	---	117.6 ± 1.0	79.5 ± 1.0

[a]Five significant figures given for calculation purposes only.

[b]Largely from Appendix V.

ACIDIC SOLUTIONS



BASIC SOLUTIONS

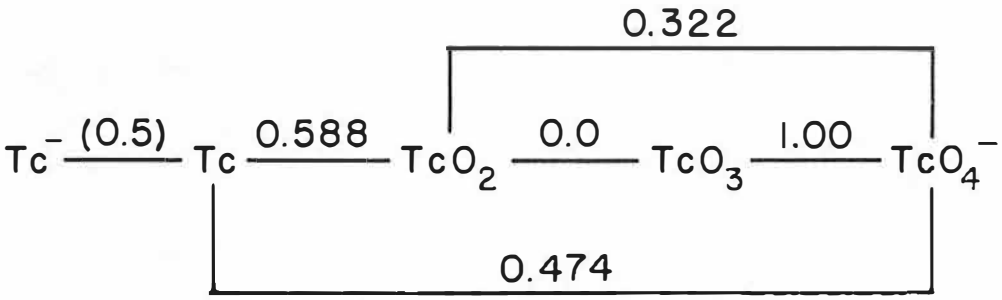


FIGURE 12.- OXIDATION - REDUCTION DIAGRAM FOR TECHNETIUM

those of the other elements, although it resembles rhenium somewhat more closely. A summary of some of the physical and thermodynamic properties of this group is given in Table XIX.

The oxidation-reduction potentials for the members of subgroup VII are summarized in Figure 13. The data for manganese are from a summary by Hugus and Latimer,[7] while the data on rhenium, with the exception of the free energy of formation of rhenium trioxide, are from Latimer's tables.[8] The data on the free energy of formation of rhenium trioxide, as well as the more dependable average for perrhenate ion based on the heat of formation of rhenium heptoxide, are from this research.

The hypothetical single bond strength of the metal atom to oxygen can be calculated from the heats of formation of the oxides. Thus, the bond energy of the rhenium-oxygen bond can be obtained by dividing the heat of formation of rhenium dioxide by four (25 kcal.), the heat of formation of rhenium trioxide by six (24 kcal.), or the heat of formation of the heptoxide by fourteen (21 kcal.). The average value of 24 kcal. will be adopted. Similarly for technetium, the values are 26, 21, and 19 kcal. from the dioxide, trioxide and heptoxide, respectively. The average value of 22 kcal. will be adopted in this case. The same method is not successful in the case of manganese because the lower oxides

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(7) Hugus, Z., and Latimer, W. M., University of California Radiation Laboratory Report, UCRL-1088, 1951.

(8) Latimer, W. M., private communication; to appear in the new edition of "Oxidation Potentials", 1952.

TABLE XIX

COMPARISON OF PROPERTIES OF SUB-GROUP VII[a]

Property	Mn	Tc	Re
ΔH_f^o $KMO_4(s)$	-194.4[b] kcal. mole^{-1}	-242.6	-262.4[b]
ΔH_f^o $M_2O_7(s)$	---	-266.1	-296.7[c]
ΔF_f^o $MO_4^-(aq.)$	-101.6[c] kcal. mole^{-1}	-150.6	-166.5[c]
ΔH_f^o $MO_3(s)$	---	-129.0 kcal.mole^{-1}	-146.0
ΔH_f^o $HMO_4(s)$	---	-167.4 kcal.mole^{-1}	-182.0[d]
ΔH_f^o $MO_2(s)$	-124.5[b] kcal. mole^{-1}	-102,500	-100.4[e]
$S_{25^o}^o$, Metal	7.59 e.u.[f]	6.8	7.8[g]
Dissociation Pressure of $HMO_4(s)$ at 25^o	---	0.67 mm.	0.35[d]
Ionization Potential, $M_{(g)}$	7.41 volts[h]	7.45[i]	7.85[j]
Atomic Weight	54.93	98.91	186.31
Density, Metal	7.20 g. cc.$^{-1}$(k)	11.50[l]	20.53[l]
Metallic Radius	1.291 A.[m]	1.358[l]	1.373[l]
M. P., Metal	1260^o(k)	2140[n]	3167[k]

TABLE XIX

COMPARISON OF PROPERTIES OF SUB-GROUP VII[a] (Continued)

Property	Mn	Tc	Re
M.P., $M_2O_7(s)$	-20°[o]	120	300[d]
Abundance (per 10,000 Si atoms)[p]	77	present[x]	.0041
Magnetic Susceptibility Metal x 10^6 c.g.s. units	$527_{(\alpha)}$[q]	270[r]	69[q]
Solubility of M_2S_7 in 9 M. HCl[s]	s.	s.	insoluble
$K_{s.p.}$, $KMO_4(s)$	0.66 (20°)[t]	0.44 (27°)[u]	4.4×10^{-3} (30°)[v]
M - O Bond Energy	30 kcal.	??	24
Stability of Aqueous Hexavalent State[w]	unstable	unstable	stable

[a]All technetium values from this research unless otherwise indicated.

[b]"Selected Values of Chemical Thermodynamic Properties", National Bureau of Standards, Washington, D. C., 1948-1950, Series I, II, III.

[c]Recalculated from (b) and values from Appendix IV.

[d]Smith, W. T., Jr., Line, L., and Bell, W. A., J. Am. Chem. Soc., in press (1952).

[e]Calculated from ref. c and data of Hugus, Z, and Latimer, W. H., to appear in the new edition of "Oxidation Potentials", 1952.

TABLE XIX

COMPARISON OF PROPERTIES OF SUB-GROUP VII[a] (Continued)

[f]Kelley, K. K., Bur. Mines Bull., 477 (1950).

[g]Estimated by the method given in Chapter VI.

[h]Bacher, R. F., and Goudsmit, S., "Atomic Energy States", McGraw-Hill, New York, N. Y., 1932, p. 278.

[i]Meggers, W. F., J. Research Natl. Bur. Standards, 47, 7 (1951).

[j]Meggers, W. F., ibid., 6, 1027 (1931).

[k]Hodgman, C. D., "Handbook of Chemistry and Physics", Chemical Rubber Co., Cleveland, Ohio, Twenty-Ninth Ed., 1945, p. 409.

[l]Mooney, Rose C. L., Acta. Cryst., 1, 161 (1948).

[m]Pauling, Linus, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N. Y., 1945, p. 409.

[n]Parker, G. W., and Martin, J. W., Oak Ridge National Laboratory Chemistry Division Quarterly Report, ORNL-1260 (1951).

[o]Mellor, J. W., "Treatise on Inorganic and Theoretical Chemistry", Longmans, Green and Co., New York, N. Y., Vol. 12, 1932, p. 466.

[p]Brown, Harrison, Rev. Mod. Phys., 21, 625 (1949).

[q]Selwood, P. W., "Magnetochemistry", Interscience, New York, N. Y., 1943, p. 203.

[r]Nelson, C. M., "The Magnetochemistry of Technetium and Rhenium", Doctoral Dissertation, The University of Tennessee, 1952.

TABLE XIX

COMPARISON OF PROPERTIES OF SUB-GROUP VII[a] (Continued)

[s]Perrier, C., and Segrè, E., J. Chem. Phys., 7, 155 (1939).

[t]Estimated from data in Mellor, J. W., "Treatise on Inorganic and Theoretical Chemistry", Longmans, Green and Co., New York, N. Y., Vol. 12, 1932, p. 466.

[u]Parker, G. W., Oak Ridge National Laboratory Chemistry Division Quarterly Report, ORNL-1116 (1951).

[v]Goldin, A. S., "A Radioactive Tracer Investigation of Rhenium Chemistry", Doctoral Dissertation, The University of Tennessee, 1951.

[w]See Figure 13.

[x]Merrill, P. W., Science, 115, 484 (1952).

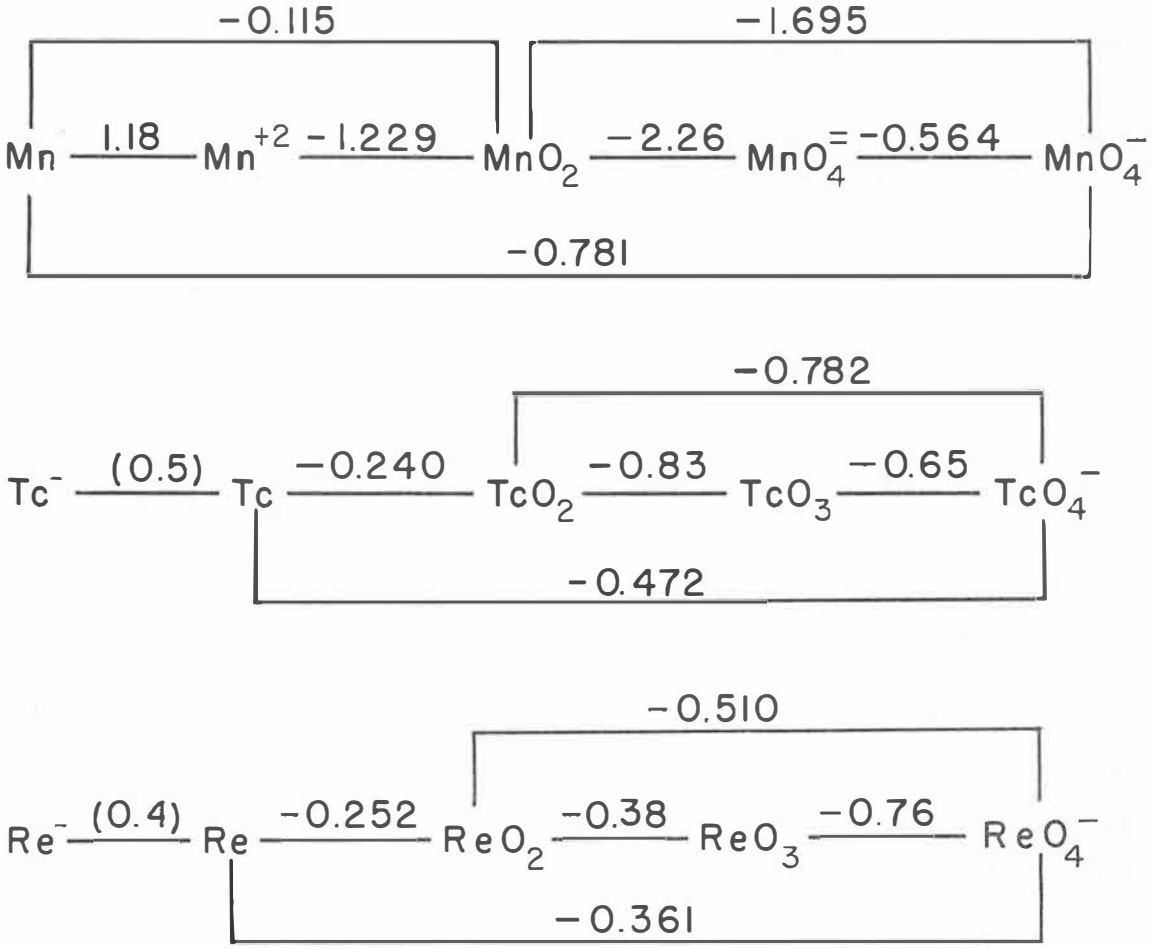


FIGURE 13.- OXIDATION – REDUCTION DIAGRAM FOR SUB-GROUP VII

have added stability over the higher oxides by reason of the partial ionic character of the oxygen-metal bonds. Thus the single bond energy for manganese(II) oxide is 46 kcal., while manganese(IV) oxide gives 31 kcal., and the manganese oxide, Mn_3O_4, gives 28 kcal. In this case, the average values from the latter two oxides will be adopted (30 kcal.) since the lower oxides of technetium and rhenium have not yet been prepared.

Since technetium resembles rhenium in many of its properties, the following differences are, perhaps, of more interest:

(1) The ionization potentials of the gaseous ions indicate that technetium is in this respect more like manganese. This is undoubtedly due to the fact that the coulombic attractive force, which is dependent upon the square of the charge, is of prime importance, the screening effect of the extra-nuclear electrons being secondary.

(2) Technetium heptoxide differs markedly from rhenium heptoxide. However, there is not enough information available on manganese heptoxide to know how technetium heptoxide resembles it, if at all. The difference between the heptoxides of rhenium and technetium undoubtedly is due to some effect in the rotational entropies of these compounds and their electrical properties near the melting points. The data seem to indicate that technetium heptoxide undergoes a type of pre-melting at low temperatures, although confirmation of this hypothesis must await a more complete study of the crystal

structure data.

(3) The data on the oxidation potentials of the rhenium trioxide couples and the estimates on the technetium trioxide couples indicate that while these two compounds are somewhat similar, rhenium trioxide is stable with respect to disproportionation while manganese(VI) and technetium trioxide are unstable in this respect.

(4) The densities and melting points of these elements are different.

(5) The solubilities of the potassium salts of the heptavalent states are different, potassium pertechnetate being the more soluble.

(6) Perrhenic and pertechnic acids, while similar in that both are unstable with respect to loss of water vapor, differ in that pertechnic acid has a relatively higher dissociation pressure than perrhenic acid at normal temperatures.

(7) The elements of sub-group VII are, of course, quite different in their abundance in the crust of the earth. No stable isotope of technetium has yet been discovered; Tc^{99} with which this research was carried out has a half-life of 2×10^5 years. Both rhenium and manganese have stable isotopes.

CHAPTER VII

SUMMARY

The new element, technetium, has been studied thermodynamically to provide data which are useful in comparing its properties with those of its neighbors in the periodic table.

The free energies and enthalpies of formation have been determined or estimated by methods of combustion calorimetry and potentiometry, and an oxidation-reduction scheme for the element has been formulated.

The thermodynamic measurements were preceeded by the preparation, purification and identification of the following compounds: (1) technetium heptoxide, (2) ammonium pertechnetate, (3) technetium dioxide, (4) pertechnic acid, and (5) technetium metal. In addition, thermodynamic information has been estimated for technetium trioxide from observations on its chemistry.

With this chemical thermodynamic information, similarities and differences between technetium and its compounds and other members of sub-group VII have been pointed out. In general, technetium has been found to resemble rhenium more closely than manganese, although a number of exceptions to this generalization have been pointed out.

The properties of this new element have again emphasized the usefulness of the periodic arrangement of elements.

Additional thermodynamic determinations have also been made on the heat of formation of rhenium heptoxide and rhenium trioxide

to supplement the data already existing in the literature on these compounds.

APPENDIXES

APPENDIX I

X-RAY DIFFRACTION POWDER PATTERNS

X-ray powder diffraction patterns have proved of value in this research to demonstrate (1) whether the same compound may be produced by different procedures, and (2) whether analogous technetium and rhenium compounds are isomorphous.[1]

A. Technetium and Rhenium Heptoxides

A comparison of the interplanar distances found in rhenium heptoxide and technetium heptoxide is afforded by Table XX. It can be seen that these two compounds are not isomorphous. The patterns are not being classified at this time and are not comparable to any other known oxide structure.

B. Technetium Metal

Mooney[2] has determined the powder pattern for technetium metal prepared by reduction of technetium sulfide with hydrogen. The metal prepared by hydrogen reduction of ammonium pertechnetate in this research gives the same pattern (see Table XXI).

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(1) The author is indebted to Mr. Ray Ellison, Chemistry Division, Oak Ridge National Laboratory, for his determinations of all of the X-ray powder patterns reported in this dissertation. Details on these structures will be published by Mr. Ellison at a future date.

(2) Mooney, Rose C. L., Acta. Cryst., 1, 161 (1948).

TABLE XX

COMPARISON OF X-RAY DIFFRACTION PATTERNS FOR TECHNETIUM AND RHENIUM HEPTOXIDES

Tc_2O_7[a]		Re_2O_7[a]	
d(A)[b]	Intensity	d(A)[b]	Intensity[c]
4.2	w[d]	3.95	w
3.72	s	3.78	s
3.42	w	3.6	m
2.80	w	3.1	m
2.74	w	2.52	m
2.52	w-	2.41	m
2.24	w	2.15	w
2.21	w	2.05	w
2.15	w+	1.90	m+
2.04	w	1.74	w+
2.01	w	1.64	w
1.88	w	1.62	w
1.79	w+	1.56	w+
1.75	w-	1.52	m
1.63	w-		
1.60	w		
1.51	w		

[a]Pattern determined by Mr. Ray Ellison, Chemistry Division, Oak Ridge National Laboratory.

[b]Interplanar distance in angstroms.

[c]Sample shows preferred orientation and accuracy of determination is poorer for certain lines.

[d]Symbols: s, strong; m, medium; w, weak.

TABLE XXI

COMPARISON OF TECHNETIUM METAL X-RAY PATTERNS

Mooney[a]		This Research[b]	
$Sin^2\theta$	Intensity[c]	$Sin^2\theta$	Intensity
0.1065	m-	0.1061	m
0.1241	m-	0.1234	m+
0.1376	vs	0.1363	vs+
0.2306	w	0.2304	w+
0.3182	m-	0.3171	m
0.3829	m+	0.3826	m
0.4237	vvw	0.4235	vw-
0.4406	s-	0.4393	m
0.4533	m	0.4531	m-
0.4930	vvw	0.4907	vvw[d]
0.5465	vw+	0.5445	vvw[d]
0.5980	vw	0.5947	vvw[d]
0.6984	m-	0.6978	m-
0.7377	vw	0.7365	w-
0.7687	s	0.7681	m+
0.8070	m	0.8068	m
0.8604	m-	0.8603	w-
0.8727	m+	0.8729	w
0.9124	w		
0.9481	m+		

[a]Mooney, R. C.L., Acta Cryst., 1, 161 (1948); metal prepared by sulfide reduction.

[b]Pattern determined by Mr. Ray Ellison, Chemistry Division, Oak Ridge National Laboratory; metal prepared by hydrogen reduction of ammonium pertechnetate.

[c]Symbols: s, strong; m, medium; w, weak; v, very.

[d]Due to faintness and location of these lines on film, poorer agreement in data so indicated is to be expected.

C. Technetium Dioxide

A comparison of the diffraction patterns for technetium dioxide prepared by pyrolysis of ammonium pertechnetate, (A), with the dioxide prepared by dehydrating at high temperatures the hydrate formed from the solution reduction of ammonium pertechnetate by zinc and hydrochloric acid, (B), is given in Figure 14. Interplanar distances are given in Table XXII for dioxide (A). It can be seen from Figure 14 that the same compound results in both cases. The hydrated dioxide has a different pattern. The distances in Table XXII do not coincide with those reported by Zachariasen[3] for a dioxide prepared by pyrolysis of ammonium pertechnetate.

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(3) Zachariasen, W. H., Argonne National Laboratory Report ANL-4082, 1947; to be published in Acta. Cryst.

TABLE XXII

INTERPLANAR DISTANCES FOR TECHNETIUM DIOXIDE[a] PREPARED BY PYROLYSIS OF AMMONIUM PERTECHNETATE

d(A.)[b]	Intensity[c]
3.363	m
3.316	vs
2.425	s
2.352	w+
2.158	w
2.109	vvw
1.874	vw
1.852	vw
1.792	vw
1.696	s-
1.668	m-
1.539	w-
1.499	w+
1.490	w+
1.461	vw
1.420	w
1.382	w+
1.366	tr
1.309	w+
1.219	w-
1.192	w+
1.171	vw

[a]Determined by Mr. Ray Ellison, Chemistry Division, Oak Ridge National Laboratory.

[b]Interplanar distance in angstroms.

[c]Symbols: s, strong; m, medium; w, weak; v, very; tr, trace.

A

B

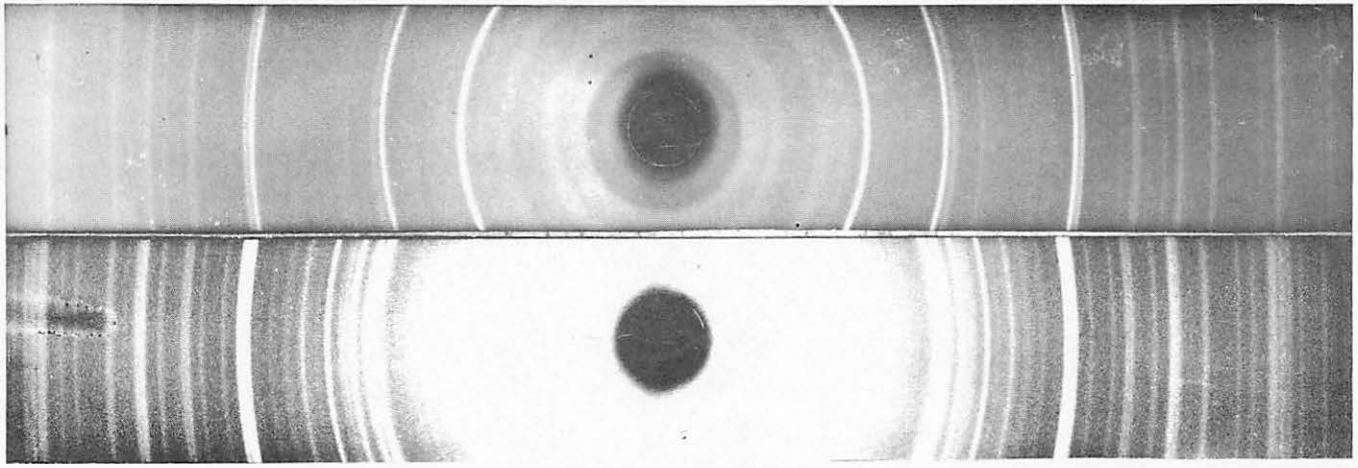


FIGURE 14.- X-RAY POWDER PATTERNS FOR TECHNETIUM DIOXIDE SAMPLES

APPENDIX II

PHYSICAL CONSTANTS

Various physical constants have been used in this research in the calculation of thermochemical quantities. Table XXIII lists the values used in all the calculations. The atomic weight of technetium has not yet been determined chemically with a high enough precision to be used as a standard; the only chemical value reported is the one from this research: 98.8 ± 0.1.[1] The calculated theoretical isotopic mass, assuming only one isotope, Tc^{99}, is 98.95.[2] The mass spectrometer value for Tc^{99} mass is 98.913.[3] Since there is no evidence at present[4] for any other long-lived isotopes of technetium formed by uranium fission, the mass spectrometer value of 98.91 will be used. None of the mass dependent values reported in this research is known to better than about one percent, so the differences in values given above are not significant.

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(1) Cobble, J. W., Nelson, C. M., Smith, W. T., Jr., and Boyd, G. E., J. Am. Chem. Soc., 74, 1852 (1952).

(2) Metropolis, N., and Reitwiesner, G., U. S. Atomic Energy Commission Document, NP-1980, 1950.

(3) Inghram, M. G., Hess, D. C., Jr., and Hayden, R. J., Phys. Rev., 72, 1269 (1947).

(4) Boyd, G. E., Record Chem. Progress (Kresge-Hooker Sci. Lib.), Spring, 1951, p. 67.

TABLE XXIII

PHYSICAL CONSTANTS

Defined calorie	=	4.1840 absolute joules[a]
	=	4.1833 int. joules[a]
Gas constant, $\underline{R}$	=	1.987 defined calories[b]
Ice point, $^{o}K.$	=	273.16[c]
ln N	=	2.303 log N
Atomic weight of Tc	=	98.91[d]
International volt equivalent	=	23,061 defined calories[c]
Atomic weights of other elements[e]		

[a]Rossini, F. D., J. Research Nat. Bur. Standards, 6, 1 (1931).

[b]Using R = 8.31436 x 10^{7} ergs $mole^{-1}$ from Bearden, J. A., and Watts, H. M., Phys. Rev., 81, 73 (1951) and the defined calorie = 4.1840 x 10^{7} ergs as given above.

[c]Birge, R. T., Rev. Mod. Phys., 12, 233 (1941).

[d]Inghram, M. G., Hess, D. C., Jr., and Hayden, R. J., Phys. Rev., 72, 1269 (1947).

[e]Committee on Atomic Weights, J. Am. Chem. Soc., 72, 1432 (1950).

APPENDIX III

TREATMENT OF THE CALORIMETRIC DATA

Figure 15 gives a typical curve obtained for the change in resistance of a platinum resistance thermometer with time when technetium was burned in the combustion calorimeter previously described (Chapter IV). Since the resistance thermometer responds linearly to the temperature over the one degree range illustrated, Figure 15 may also be considered a time-temperature curve.

The curve illustrates the salient features of time-temperature curves for such calorimeters: the initial, small, linear rise corresponds to a heat leak into the calorimeter from the bath. At the ignition time, the contents of the bomb begin to burn and supply heat to the calorimeter and the temperature then rises quite rapidly. This "rise curve" is almost exponential after the first few seconds. It then reaches a maximum value, and, depending upon whether the final temperature inside the calorimeter exceeds or is lower than that of the bath, the temperature falls or continues to rise at a small, linear rate.

The problem is, what part of the temperature change should be attributed to the heat of combustion and what part to radiation leakage? One simple method is to take, at some arbitrary time, the difference between the extrapolations of the initial and final linear portions of the curve. However, the net rise will then depend upon the time at which it is computed, since, in general, the slopes of the two linear portions will not be the same. If the "rise curve"

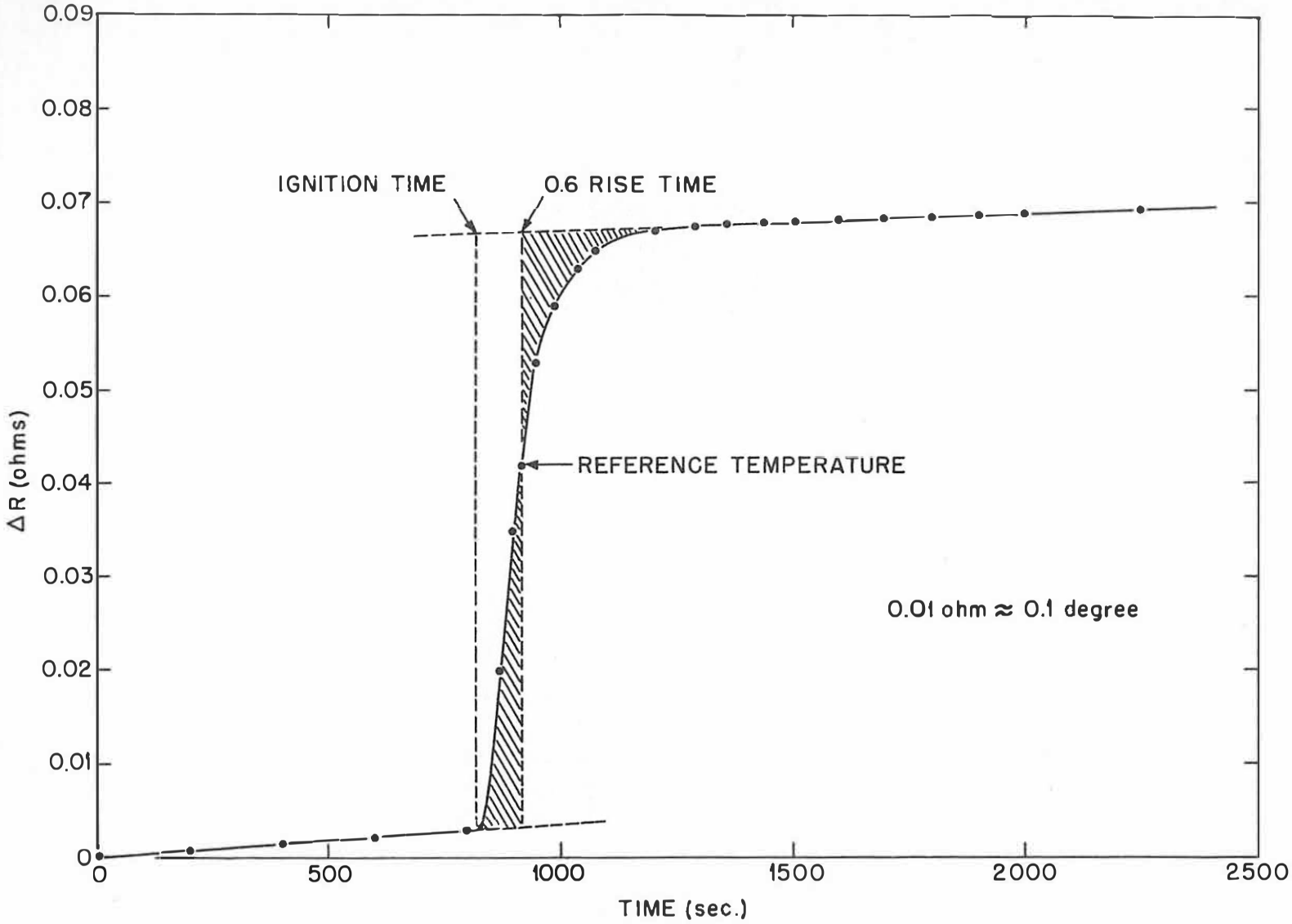


FIGURE 15.- TIME-TEMPERATURE CURVE FOR CALORIMETER

were symmetrically shaped, the net temperature change could be taken at a time corresponding to the inflection point.

It has been found experimentally by Dickinson[1], however, that most of the calorimeter "rise curves" are exponential after the first few seconds after firing. When this is the case it is recommended that the net temperature change be taken at a time such as to give equal areas under the rise-time curve (Figure 15). For an ideal exponential curve this would correspond to 0.63 times the total net rise, but for most practical calorimeters, it corresponds to about 0.60 times the net rise. This time can be determined either empirically or analytically. The 0.6 rise-time method was used for the calculation of all net calorimetric temperature changes in both the combustion and solution calorimeters.

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(1) Dickinson, H. C., U. S. Bur. Standards Bull., 11, 189 (1914).

APPENDIX IV

THE HEATS OF COMBUSTION OF RHENIUM AND RHENIUM TRIOXIDE

To test the accuracy of the combustion calorimeter rhenium metal was burned as described previously (Chapter IV). The heat of combustion of rhenium in oxygen has been determined by Roth and Becker.[1] Since technetium and rhenium are similar, the latter appeared to be the best available secondary standard to test the calorimetric equipment. The heat of combustion of rhenium trioxide to form rhenium heptoxide was also measured, since the only data previously available on this compound were reported by Roth and Becker who used indirect methods. More accurate heat data on rhenium trioxide were desired to assist in estimating some of the thermodynamic properties of technetium trioxide, which has not yet been prepared in large enough quantities to burn.

A. Heat of Combustion of Rhenium Metal

Rhenium metal,[2] prepared by hydrogen reduction of ammonium perrhenate at 500°, was used directly. It was found that rhenium burned somewhat more easily than technetium metal, and because of its higher density and compactness, less oil accelerator was required.

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(1) Roth, W. A., and Becker, G., Z. physik. Chem., A 159, 27 (1932); data has been recalculated and summarized in "Selected Values of Chemical Thermodynamic Properties", U. S. Bureau of Standards, Washington, D. C., 1948, Series I.

(2) Kindly furnished by the Rhenium Plant, The University of Tennessee.

The data obtained using about 100 mg. samples are given in Table XXIV. Taking 186.31 as the atomic weight of rhenium, and 1397.1 cal.deg.$^{-1}$ as the heat capacity for the calorimeter (as given in Chapter IV), the heat of combustion estimated from Table XXIV becomes -149.3 ± 0.2 kcal. mole^{-1} of Re, or -298.6 ± 0.4 kcal. mole^{-1} of Re_2O_7. The process measured was:

$$2Re(s) + 7/2\ O_{2(g,30\ atm.)} + H_2O_{(l)} + aq. = 2HReO_4(\overline{M.}) \qquad \text{(A IV-1)}$$

$$\Delta E = -298.6 \pm 0.4 \text{ kcal.}$$

where $\overline{M}$. represents the average perrhenic acid concentration in the resulting bomb solution. Due to the lower volatility of rhenium heptoxide compared with technetium heptoxide, only about one-half of the products of the rhenium combustion went into the bomb solution. The remainder was found in the ignition cup as fused heptoxide. Because of the relatively low saturation pressure of water vapor in the gas at 30 atm., the heptoxide apparently did not absorb water during the run.

As with technetium, corrections to: (1) standard state conditions of unit fugacity for the oxygen and for (2) change of the measured ΔE into the corresponding ΔH of combustion must be made (See Chapter IV):

$$2Re(s) + 7/2\ O_{2(g)} + H_2O_{(l)} + aq. = 2HReO_4(\overline{M.}) \qquad \text{(A IV-2)}$$

$$\Delta H = -300.9 \pm 0.4 \text{ kcal.}$$

TABLE XXIV

HEAT OF COMBUSTION OF RHENIUM METAL

$\Delta T_{obs.}$	$\Delta T^{a}_{corr.}$	Wt. oil	ΔT_{oil}	ΔT_{net}	Wt. Re	Temp. Rise $g.^{-1}$
0.6561°	0.6514°	73.01 mg.	0.5775°	0.0739°	129.09 mg.	0.573° $g.^{-1}$
0.4511	0.4464	49.24	0.3895	0.0569	98.77	0.576
0.6214	0.6167	69.93	0.5532	0.0635	111.00	0.572
					Average:	0.574 ± 0.001° $g.^{-1}$

[a]Corrected for fuse ignition and nitric acid formation.

The heat of combustion of the metal to form anhydrous rhenium heptoxide was calculated on the basis that half of the heptoxide dissolved in the water in the bomb to form a 0.1 M. solution of perrhenic acid. Using 5 kcal. for the heat of solution of a half-mole of rhenium heptoxide to form a 0.1 M. perrhenic acid solution[3] the following is obtained:

$$2Re(s) + 7/2\ O_{2(g.)} = Re_2O_7(s) \qquad \text{(A IV-3)}$$
$$\Delta H = -295.9 \pm 2.0 \text{ kcal. mole}^{-1}$$

Any error is largely due to the uncertainty about the final state of rhenium heptoxide. This value may be compared with that given by the Bureau of Standards[4] of -297.5 ± 2.0 kcal. mole^{-1}. The agreement is considered satisfactory; for subsequent calculations the average value, -296.7 ± 0.8 kcal. mole^{-1}, will be used.

B. The Heat of Combustion of Rhenium Trioxide

Rhenium trioxide[5] was also burned in the same manner as was rhenium metal. Very little heat was given off (Table XXV). In fact, after the "oil heat" was subtracted, the remaining temperature rise was barely outside the experimental errors involved, indicating that

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(3) Estimated from the data given by Roth, W. A., and Becker, G., Z. physick. Chem. A 159, 27 (1932).

(4) "Selected Values of Chemical Thermodynamic Properties", U. S. National Bureau of Standards, Washington, D. C., 1948, Series I.

(5) Kindly furnished by the Rhenium Plant, The University of Tennessee, Knoxville, Tennessee.

TABLE XXV

THE HEAT OF COMBUSTION OF RHENIUM TRIOXIDE

$\triangle T_{obs.}$	$\triangle T^{a}_{corr.}$	Wt. oil	$\triangle T_{oil}$	$\triangle T_{net}$	Wt. ReO_3 [b]	Temp. rise $g.^{-1}$
0.9267°	0.9220°	116.26 mg.	0.9196°	0.0024°	253.1 mg.	0.0095° $g.^{-1}$
1.1438	1.1391	142.97	1.1309	0.0082	253.7	0.0323
0.6245	0.6198	78.26	0.6190	0.0008	78.3	0.0103
					Average:	0.0174 ± 0.0080

[a] Corrected for fuse ignition and nitric acid formation.

[b] This represents about 80-90 percent of the charge; the amount actually burned was obtained from the loss in weight of the combustion sample.

the difference between the heats of formation for the trioxide and heptoxide is very small per rhenium atom. The fraction of rhenium trioxide burned, which was determined by loss in weight of the rhenium trioxide sample amounted to about 80-90 percent. The process measured was:

$$2ReO_{3(s)} + \tfrac{1}{2}O_{2(g,\ 30\ atm.)} + H_2O_{(l)} + aq. = 2HReO_4(\overline{M.}) \qquad \text{(A IV-4)}$$

$$\Delta E^1 = -11.4 \pm 6.0 \text{ kcal.}$$

Taking the value of 0.0174 deg. $g.^{-1}$ from Table XXV (4.08 deg. $mole^{-1}$ of ReO_3), and using the value of 1389.1 cal. $deg.^{-1}$ for the heat capacity of the calorimeter (see Chapter IV) the heat of reaction for (A IV-4) becomes -5.7 ± 3.0 kcal. $mole^{-1}$ of ReO_3 or -11.4 ± 6.0 kcal. $mole^{-1}$ of Re_2O_7 formed.

As before, it was found that only half of the rhenium heptoxide formed went into solution. After making the corrections for the standard state of the oxygen, changing from ΔE to ΔH, and subtracting 5 kcal. for the heat of solution of half a mole of rhenium heptoxide, the following was obtained:

$$2ReO_{3(s)} + \tfrac{1}{2}O_{2(g)} = Re_2O_{7(s)} \qquad \text{(A IV-5)}$$

$$\Delta H_5 = -6 \pm 6 \text{ kcal.}$$

The heat of formation of rhenium trioxide may now be calculated from its heat of combustion, and the heat of formation of rhenium heptoxide, -296.7 kcal. $mole^{-1}$:

$$\triangle H^{\circ}_{f(ReO_3)} = \tfrac{1}{2}\left[\triangle H^{\circ}_{f(Re_2O_7)} - \triangle H_5\right] = -146 \pm 3 \text{ kcal. mole}^{-1} \qquad \text{(A IV-6)}$$

Roth and Becker obtained -83 kcal. mole^{-1} for this heat of formation. The poor agreement is due to the fact that their calculation was based upon the differences observed when rhenium was burned to form a mixture containing the heptoxide and varying amounts (4-8 percent) of the trioxide. The direct determination reported here is considered more accurate.

APPENDIX V

ESTIMATION OF ENTROPY VALUES FOR TECHNETIUM AND ITS COMPOUNDS

The heat and cell EMF data obtained in this research can be made more useful by the estimation of suitable entropy values for technetium and its compounds. Thus, by the relation:

$$\Delta F = \Delta H - T \Delta S \qquad \text{(A V-1)}$$

free energy data can be estimated from calorimetric heats of reaction, and the heats of formation and reaction can be calculated in turn from cell voltages (free energy changes). These estimations are utilized in the calculation and estimation of many thermodynamic quantities given in Chapter VI.

A. The Entropy of Technetium Metal

The entropy of technetium metal can be estimated rather accurately from its position in the periodic table. Plotting the entropies[1] of the transition elements at 25° against their atomic numbers, it was observed that each period formed a parabolic shaped curve, with manganese, technetium and rhenium forming the vertex for each period. The entropy of technetium metal was estimated to be 6.8 cal. $mole^{-1}$ $deg.^{-1}$ (e.u.) by this empirical method. This may be compared with the value estimated by Brewer[2] of 8 e.u.

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(1) Kelley, K. K., U. S. Bur. of Mines Bull. 477, 1950.

(2) Brewer, Leo, Paper 3 in "Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics", edited by L. L. Quill, McGraw-Hill, New York, N. Y., 1950.

B. The Entropy of $TcO_{4(aq.)}^-$

Latimer[3] has shown that the entropies of simple ions (assuming $H^+_{(aq.)} = 0$) can be represented by the equation

$$S^o = 3/2\ R \ln M + 37 - 270\ Z/r_e^2 \qquad \text{(A V-2)}$$

where M is the mass of the ion in atomic weight units, Z is its charge in e.s.u., and r_e is the effective ionic radius. For simple ions, r_e can be calculated from the ionic crystal radii. It is known that perchlorate, perrhenate and pertechnetate ions are isomorphous and that their ions can be coprecipitated from solution. If it is assumed that equation (A V-2) also holds for XO_4^- ions, and that Z/r_e^2 is the same for TcO_4^-, ReO_4^- and ClO_4^-, then on using the value for the entropy of the ClO_4^- ion as 43.6 ± 0.5 e.u.,[4] the entropies of $TcO_{4(aq.)}^-$ and $ReO_{4(aq.)}^-$ are calculated to be 45.1 and 46.4 e.u., respectively.

C. The Entropy of $KTcO_{4(s)}$

Knowing the value for the entropy of the $TcO_{4(aq.)}^-$ ion the entropy of $KTcO_{4(s)}$ may be calculated using the solubility measurements of Parker.[5] Using his value for the $K_{s.p.}$ at 7° of 0.14 and

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(3) Powell, R. E., and Latimer, W. M., J. Chem. Phys., 19, 1139 (1951).

(4) Kelley, K. K., U. S. Bur. of Mines Bull., 477, 1950.

(5) Parker, G. W., Oak Ridge National Laboratory Chemistry Division Quarterly Report, ORNL-1116, 1951; see also Table XVII.

0.44 at 27°, the heat of solution is 9550 cal. mole^{-1}, and ΔF at 27° is $-RT \ln K_{s.p.}$ = 490 cal. mole^{-1}. ΔS^{o} can then be estimated to be 30.2 e.u. for the process:

$$aq. + KTcO_{4(s)} = K^{+}_{(aq.)} + TcO^{-}_{4(aq.)} \qquad (A\ V\text{-}3)$$

$$\Delta S^{o} = 30.2$$

As is usually done for this type of calculation, corrections for dilution of the saturated solution to infinite dilution have been neglected, as well as the change from 27° to 25°. Taking the $K^{+}_{(aq.)}$ entropy as 24.2 e.u.[6] then S^{o} for $KTcO_{4(s)}$ becomes 39.1 e.u.

The entropy of $KTcO_{4(s)}$ was also estimated from the entropy of $KClO_{4(s)}$ using the equation proposed by Latimer[7] for similar substances:

$$S^{o}_{KClO_4} - S^{o}_{KTcO_4} = 3/2\ R \ln \frac{\text{at. wt.}_{(Cl)}}{\text{at. wt.}_{(Tc)}} \qquad (A\ V\text{-}4)$$

Using the value of 36.1 e.u. for the entropy of $KClO_{4(s)}$[8], the entropy of $KTcO_{4(s)}$ calculated from equation (A V-4) was again 39.1 e.u.

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(6) Kelley, K.K., U. S. Bur. Mines Bull., 477, 1950.

(7) Latimer, W. M., "Oxidation Potentials", Prentice-Hall Pub. Co., New York, N. Y., 1938, p. 328.

(8) Kelley, K. K., loc. cit.

D. Entropies of Solid Technetium Compounds of the Formula $MTcO_4$

Latimer[9] has shown that the entropies of solid ionic compounds may be assigned in an additive manner to the cation and anion. The contributions of all of the common ions have been averaged into consistent values and, hence, the entropy of many solid compounds can be estimated with fair accuracy. Thus, the entropy of $KClO_{4(s)}$ is equal to $S^o_{K^+_{(s)}} + S^o_{ClO_{4(s)}^-} = 9.2 + 26.0 = 35.2$ e.u. which may be compared to the experimental value of 36.1 e.u.[10]. Using 39.1 e.u. for $KTcO_{4(s)}$ as given above, and 9.2 e.u. for $K^+_{(s)}$[11], the calculated contribution of $TcO_{4(s)}^-$ in solid salts is 29.9 e.u. Using 13.9 e.u. for $NH^+_{4(s)}$, 0.0 for $H^+_{(s)}$ and 7.4 for $Na^+_{(s)}$[12] from Latimer's table, then the entropies of $NH_4TcO_{4(s)}$, $HTcO_{4(s)}$ and $NaTcO_{4(s)}$ at 25° are 43.8, 29.9, and 37.4 e.u. respectively.

E. The Entropy of K_2TcCl_6

The entropy of potassium hexachlorotechnetate(IV) may be calculated by comparing it with the general class of salts of the type K_2MCl_6, and breaking up the total entropy into that of the component elements. Using[13] 18.4 for K_2, 48.6 for Cl_6 and 12.5 for technetium,

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(9) Latimer, W. M., J. Am. Chem. Soc., 73, 1480 (1951).

(10) Kelley, K. K., U. S. Bur. Mines Bull., 477, 1950.

(11) Latimer, W. M., op. cit.

(12) Latimer, W. M., loc. cit.

(13) Latimer, W. M., loc. cit.

the entropy of K_2TcCl_6 is 79.5 e.u. at 25°. The value of 12.5 e.u. for the contribution of technetium in its compounds is based upon Latimer's[14] empirical curve for metallic atoms in compounds, and not upon the absolute entropy of technetium (6.8 e.u.).

F. Entropies of Technetium Oxides

Using the same additivity principles, the entropies of oxides may be calculated with some accuracy. In this case, however, the contribution by the oxygen atoms to the total entropy depends upon the coordination number of the metallic constituent, since the bond distances and stabilities of the various oxides of the same element will be, of course, somewhat different. The average contributions for oxygen in the oxides of the type MO_2, MO_3 and M_2O_7 have been estimated from oxides for which entropy data are available.[15] Thus, the entropy of TcO_2 becomes 12.5 + 2(1.2) or 14.9 e.u., TcO_3 is 12.5 + 3(1.1) or 15.7 e.u., and Tc_2O_7 (calculated as twice $TcO_{3.5}$) is 2(12.5) + 7(2.65) or 43.5 e.u. This latter value may be considerably in error because of the paucity of data for the higher oxides. The entropy of fusion (see Chapter III) for this compound indicates that it may have an abnormally low entropy at room temperature. Therefore, the value calculated from equation (VI-12) and

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(14) Latimer, W. M., J. Am. Chem. Soc., 73, 1480 (1951).

(15) Kelley, K. K., U. S. Bur. Mines Bull., 477, 1950.

based upon the entropy of $HTcO_{4(s)}$ will be used: 39.0 e.u.

G. The Entropy of $Tc_{(g)}$

The entropy of gaseous technetium at 25° has been calculated from the equation:[16]

$$S^{o} = S^{o}_{trans.} + S^{o}_{e} \qquad \text{(A V-4)}$$

where $S^{o}_{trans.}$ is the translation entropy for a monatomic gas and is given by the Sakur equation as 3/2 R ln M + 25.996. S^{o}_{e} is the entropy associated with the electronic multiplicity of the ground state of the technetium atom. This ground state is a $^{6}S_{5/2}$ level;[17] thus the multiplicity, p = 2j + 1, is (2) 5/2 + 1 or 6. S^{o}_{e} is equal to R ln p, or 3.561 e.u. $S^{o}_{trans.}$ has the value of 39.694; therefore, the total entropy at 25° is 43.26 ± 0.01 e.u. The other energy levels for the atom are too far above the ground state (the lowest is 2572.9 $cm.^{-1}$ above the ground state) to contribute to the entropy at room temperatures.

The various entropies calculated and estimated for technetium and its compounds are summarized in Table XXVI. For other entropies based upon measurements performed in this research but also involving the entropies estimated in this appendix, see Chapter VI.

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(16) Kelley, K. K., U. S. Bur. Mines Bull., 477, 1950.

(17) Meggers, W. F., J. Research Nat. Bur. Standards, 47, 7 (1951).

TABLE XXVI

SUMMARY OF ENTROPIES ESTIMATED FOR TECHNETIUM AND SOME OF ITS COMPOUNDS[a]

Compound	$S^{o}_{25^{o}}$
$Tc_{(g)}$	43.26 ± 0.01 e.u.[b]
$Tc_{(s)}$	6.8 ± 0.2
TcO_4^- (aq.)	45.1 ± 0.4
$KTcO_{4(s)}$	39.1 ± 1.0
$NH_4TcO_{4(s)}$	43.8 ± 1.0
$HTcO_{4(s)}$	29.9 ± 2.0
$NaTcO_{4(s)}$	37.4 ± 1.0
$K_2TcCl_{6(s)}$	79.5 ± 1.0
$TcO_{2(s)}$	14.9 ± 0.5
$TcO_{3(s)}$	15.7 ± 0.6
$Tc_2O_{7(s)}$	39.0 ± 2.0[c]

[a]See also Table XVIII.

[b]Errors estimated from deviations observed using the same method of estimation for compounds of known entropies.

[c]The error for this compound may be larger because of the abnormality observed in its entropy of fusion (See Chapter III).

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VITA

James W. Cobble was born in Kansas City, Missouri, on March 15, 1926. He attended the elementary schools of this city and was graduated from San Diego High School in San Diego, California in June, 1942. The following two years he attended San Diego State College, leaving to join the US Naval V-12 unit at Arizona State College at Flagstaff, Arizona in March, 1944. In March, 1945, he entered the US Naval Midshipman's School at the University of Notre Dame, and was commissioned an Ensign, USNR in July, 1945. He served with the Pacific Fleet until May, 1946, receiving his B. A. degree from Arizona State (in absentia) in February, 1946.

He attended the University of California at Berkeley, California from September, 1946 until September, 1947. He entered the Graduate School of the University of Southern California at Los Angeles, California in September, 1947 and received the M.S. degree in Chemistry from that institution in June, 1949. During his tenure at that school, he held successively the positions of teaching assistant, research assistant, and research fellow.

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