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

Thermodynamic Properties of Technetium and Rhenium Compounds. II. Heats of Formation of Technetium Heptoxide and Pertechnic Acid, Potential of the Technetium(IV)–Technetium(VII) Couple, and a Potential Diagram for Technetium[1,2]

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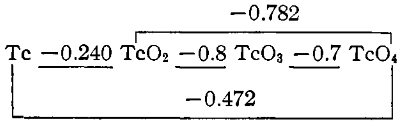
The thermodynamics of technetium and some of its compounds have been studied by semimicro calorimetry and potentiometry using milligram quantities of the element. The heat of formation of Tc_2O_7(c) was -266.1 ± 2.6 kcal. mole^{-1}, and the potential of the TcO_2–TcO_4^- electrode was -0.782 ± 0.011 volt. When combined with suitable experimental and estimated entropy values, some thirty thermodynamic functions could be calculated for technetium and its compounds. The resultant oxidation–reduction diagram in acid solution is shown.



Introduction

Heats of formation and solution of technetium heptoxide and the potential of the technetium dioxide–pertechnetate ion couple have been measured in a continuation of studies on the thermodynamic properties of technetium compounds.[4] In addition, heats of formation were computed for a number of other technetium compounds, and, using suitable estimates of the necessary entropy values, free energies of formation were evaluated. An oxidation–reduction diagram of the relations of the various technetium couples was constructed from the cell measurements and free energies, and this proved useful in comparing the closely similar chemistries of technetium and rhenium.

Experimental

Technetium metal was isolated following a procedure already described.[5] Final purification steps consisted in burning the metal to form heptoxide, sublimation of the latter, neutralization of the pure sublimate with aqueous ammonium hydroxide, evaporation to solid ammonium pertechnetate and, lastly, hydrogen reduction of the ammonium salt to the free metal at elevated temperatures.

Technetium heptoxide was prepared by burning the metal in dry oxygen.[6] Varying amounts of this product were then vacuum distilled into small, thin-walled glass bulbs which were sealed *in vacuo*. In performing the heat of solution measurements these bulbs were crushed in the calorimeter, and the amount of technetium heptoxide they contained was determined from the weight of ammonium salt found on evaporating the neutralized calorimeter solution.

Technetium dioxide was prepared in three different ways, based upon known methods for the preparation of rhenium dioxide.[7,8] The two samples used in the cell measurements were made by the reduction of an aqueous ammonium pertechnetate solution by zinc and hydrochloric acid,[9] and by electrodeposition onto platinum gauze from acid ammonium pertechnetate solution. The black product formed in the latter instance was not identified chemically, but since the cell potentials were the same with both preparations when the acid pertechnetate–dioxide couple was measured, it may be assumed that the preparations gave essentially the same material.

Pyrolysis of ammonium pertechnetate at elevated temperatures[10] gave a third product which chemical analysis showed corresponded closely to TcO_2.[11] The potentials of the cells in which it was used, however, were neither steady nor entirely reproducible from sample to sample. Further, the X-ray diffraction pattern[9] differed from that for the zinc–hydrochloric acid reduced material. Accordingly, none of the results reported below were obtained with this preparation.

Apparatus.—Heat of combustion measurements were conducted in a small calorimeter consisting of a semi-micro type combustion bomb submerged in water contained in a one liter glass dewar (Fig. 1). Temperature rises were determined with a calibrated, glass-enclosed resistance thermometer. The top of the calorimeter was closed off by a cover plate which could be bolted onto a flanged copper ring cemented to the dewar so that the whole assembly could be immersed in a constant temperature water-bath. The resistance thermometer, glass stirring rod and ignition wire entered the calorimeter through three vertical copper tubes which pierced the cover plate. The microcombustion bomb,[12] which was of 50-ml. internal volume, carried an inlet–outlet valve and two ignition terminals, and was suspended in the dewar 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 ensure a constant heat-leak from the calorimeter, a radiation shield also was provided. This shield consisted of an inverted copper cup which fitted snugly into the dewar confining the principal heat-leak between two copper surfaces about 2 cm. apart. This design is in accord with the recommendations of White.[13] 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 to provide for the rapid mixing of the water. The propeller was rotated at 1500 r.p.m. by a synchronous motor.

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(1) Presented before the Division of Physical and Inorganic Chemistry, 121st Meeting, American Chemical Society, March 23–26, 1952, Buffalo, N. Y.

(2) This work was performed for the Atomic Energy Commission.

(3) From the thesis of J. W. Cobble submitted to the Graduate School of the University of Tennessee in partial fulfillment of the requirements for the Ph.D. degree in June, 1952.

(4) W. T. Smith, Jr., J. W. Cobble, and G. E. Boyd, THIS JOURNAL, **75**, 5773 (1953), paper I of this sequence.

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

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

(7) N. V. A. Briscoe, D. L. Robinson and E. M. Stoddard, *J. Chem. Soc.*, 668 (1931).

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

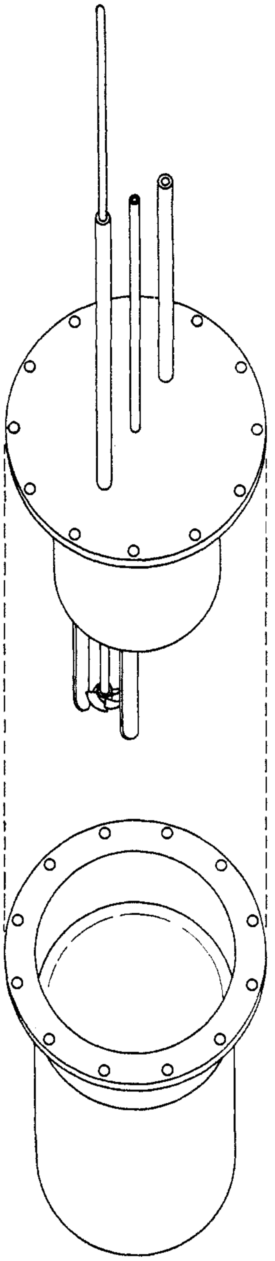
(9) C. M. Nelson, G. E. Boyd and W. T. Smith, Jr., to be published; C. M. Nelson, doctoral thesis, University of Tennessee, 1952.

(10) S. Fried, private communication, 1950.

(11) J. W. Cobble, doctoral thesis, University of Tennessee, 1952.

(12) Model 1103, Parr Instrument Company, Moline, Ill.

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



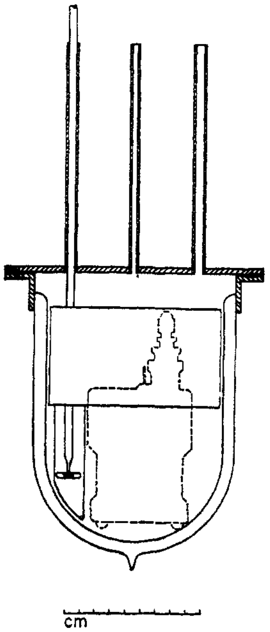


Fig. 1.—Combustion calorimeter.

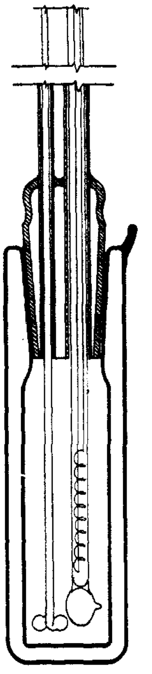


Fig. 2.

The calorimeter assembly was submerged in a water-bath at 25° 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% 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 ohm, corresponding to about ±0.0005°. The corrected temperature rise in the calorimeter was computed by the Dickinson method.[14] Since the 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.

Samples up to 100 mg. of technetium metal, formed by ammonium pertechnetate reduction, were burned in 30 atm. of oxygen with about 60 mg. of paraffin oil accelerator. The fuse assembly consisted of a measured length of cotton thread suspended from a platinum wire and extending into the oil–metal combustion charge.

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

The nitric acid formed from traces of nitrogen in the oxygen amounted to 0.0131 meq., corresponding to a temperature rise of 0.00016°.[15] Since the same amount of acid was always formed regardless of the size of the oil charge, it was assumed that this also corresponds to the amount of nitric acid formed in the oil–technetium burning. The fuse and nitric acid correction was 0.0047 ± 0.0001°. The heat of combustion of the oil itself was determined by many separate experiments.

The heat capacity of the calorimeter was determined by the combustion of Bureau of Standards benzoic acid (sample 39f), quoted to have a standard heat of combustion of 26.4284 international kilojoules g.$^{-1}$; corrected to bomb conditions this was 26.4279 int. kj. g.$^{-1}$ or 6317.48 cal.[16] The temperature rise on combustion of 100-mg. samples in the calorimeter was found to be 4.521 ± 0.006° on four determinations. After correcting for the fuse and nitric acid heat, the heat capacity of the calorimeter was found to be 1397.4 cal. deg.$^{-1}$.

The oil accelerator was required to obtain combustion of the technetium metal as had been found for rhenium by Roth and Becker.[17] The oil had a heat of combustion of 7.910 ± 0.018 deg. g.$^{-1}$ (11.04 kcal. g.$^{-1}$) based on nine determinations; this value was *not* corrected using the Washburn[15] corrections because of the level of accuracy of the experiments. In the case of the technetium–oil mixtures, two corrections were made: the temperature rise due to the ignition process, and that due to the amount of oil accelerator used.

The precision of the instrument seemed to be determined solely by the magnitude of the temperature rise and, hence, by the precision of the resistance thermometer measurements. This precision corresponded to about ±0.0005°, so that with a sample giving a temperature rise of about 0.5°, as in the case of the paraffin oil used to burn the technetium, as well as in the benzoic acid calibration, the precision was found to be about 0.1–0.2%. However, with the samples of technetium available (30–100 mg.), the temperature rise due to the technetium combustion alone was only about 0.05°; consequently, the errors involved in the heat of formation were much larger, about 1–2%. The standard deviation was taken as $S = \sqrt{\Sigma(\Delta x)^2/n(n-1)}$ where $\Sigma(\Delta x)^2$ represents the sum of the squares of the deviations of the determinations from the average of n determinations.[18]

The technetium heptoxide from the technetium combustion dissolved in the water formed on the combustion of the oil to give a very concentrated solution of pertechnic acid. Because of the limited quantities of technetium available, heat of dilution studies could not be made readily on such small amounts of relatively concentrated solutions. Therefore, 2.00 ml. of water was initially placed in the bomb so that the final product would be a more dilute solution of pertechnic acid. This solution was then used for further heat of dilution studies.

The calorimeter and associated equipment were tested by repeating the similar experiments of Roth and Becker on the heat of formation of rhenium heptoxide from rhenium combustions.[17] These data in which agreement is satisfactory are reported in another communication.[19]

The heat of solution calorimeter was used to measure the heat of solution of technetium heptoxide and the heat of dilution of pertechnic acid solutions. This calorimeter (see Fig. 2) was constructed from a small cylindrical glass dewar

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(14) H. C. Dickinson, *Nat. Bur. Standards Bull.*, **11**, 189 (1914).

(15) E. W. Washburn, *J. Research Natl. Bur. Standards*, **10**, 525 (1933).

(16) One calorie has been taken as equal to 4.1833 joules (int.).

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

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

(19) G. E. Boyd, J. W. Cobble and Wm. T. Smith, Jr., THIS JOURNAL, **75**, 5783 (1953), paper III.

4.25 in. long and 1.5 in. in diameter. It was fitted with a standard taper joint so that a glass top could be fitted onto it. Two glass tubes were sealed vertically into the top, providing inlets for the platinum resistance thermometer and the glass stirrer. The calorimeter was submerged in a bath controlled to ±0.002° during the run.

This calorimeter was calibrated by the neutralization of an aqueous sodium hydroxide solution with a slight excess of hydrochloric acid. 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.[20] The water equivalent of this calorimeter was 39.69 ± 0.09 cal. deg.$^{-1}$ at 25°.

Between 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 thermometer was measured as before. For heat of dilution experiments, the solution was placed in a sealed bulb and broken in the calorimeter water.

Cell Potentials.—The acid half-cell was contained in 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 hold the technetium dioxide. A glass stirrer extending into the cell was rotated slowly during the measurements to minimize polarization of the electrode. The cell solution of pertechnic acid was made by dilution of a more concentrated, standardized solution. This concentration was 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,[21] to a silver–silver chloride half-cell of known voltage. The two half-cells were immersed in a thermostat which was maintained to within ±0.05° at 25°. The voltage of the cell was measured periodically for several days 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.

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 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 of the finely-divided technetium oxide to become mixed 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 in the acid cell. However, difficulty was experienced in getting the technetium dioxide to stay in the cup, since it apparently disintegrates 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. When nitrogen gas was passed through the cell to exclude carbon dioxide, the voltage still was not constant. It was also observed previously with 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 for the basic cell were taken during the first few hours.

Below a concentration of about 0.06 *M* TcO_4^-, the basic cell voltage was neither steady nor reproducible. Since technetium was not available for more concentrated solutions, it was not possible to make a concentration study, and the voltage obtained for this cell is, therefore, considered only approximate.

Experimental Results

Calorimetry.—Only 80–90% of the technetium metal in the charge could be burned, regardless of the design of the ignition cup or total oxygen pressure. This is somewhat less than for rhenium.[17,19] The residue after ignition was essentially pure metal, as demonstrated by weighing and taking mass balances of all of the technetium in the bomb. Eighty-five to ninety per cent. of the technetium was found in the bomb solution, and the rest was as pertechnic acid of various concentrations on the top and sides of the inside of the bomb. In the calculations, an average (0.3 mole l.$^{-1}$) of the acid concentrations resulting from all of the combustions is used. The heat data are given in Table I. Using 1397.4 cal. deg.$^{-1}$ for the water equivalent of the calorimeter, the energy is

$$2Tc(c) + 7/2O_2(g, 30\ atm.) + H_2O(l) + aq. = 2HTcO_4(0.3\ M)$$

$$\Delta E = -276.0 \pm 2.8\ \text{kcal.} \qquad (1)$$

The atomic weight of technetium has been arbitrarily taken as 99.00, although theoretical calculations[22] and physical measurements[23] show it to be somewhat smaller. Errors caused by this adoption are negligible (~0.1%).

TABLE I

HEAT DATA FOR COMBUSTION OF TECHNETIUM METAL

$\Delta T_{cor.}$,[24] deg.	ΔT_{oil}, deg.	ΔT_{net}, deg.	Wt. Tc, mg.	Temp. rise, deg. g.$^{-1}$
0.6598	0.6293	0.0305	31.01	0.983
.7787	.7501	.0286	29.25	0.979
.9070	.8499	.0572	56.39	1.014
1.1479	1.0699	.0780	76.25	1.023
0.6197	0.5757	.0440	45.38[25]	0.969
1.2445	1.1438	.1007	99.00[25]	1.018
			Average	0.998 ± 0.009 deg. g.$^{-1}$

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[20] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943, p. 541.

[21] K. V. Grove-Rasmussen, *Acta Chem. Scand.*, **5**, 422 (1951).

[22] N. Metropolis and G. Reitwiesner, U. S. Atomic Energy Commission Document NP-1980, 1950.

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

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

[25] Samples so indicated had been degassed at 800° for 2–3 hours *in vacuo*.

Two of the samples of technetium metal had been degassed at high temperatures *in vacuo* following their preparation from ammonium pertechnetate reduction. Since the experimental heats of combustion of these two samples were, within experimental error, the same as for the other nondegassed samples, it was concluded that technetium prepared in this manner does not contain hydrogen to any appreciable extent.

Correcting eq. 1 to unit fugacity oxygen pressure,[26] and using $\Delta n = -7/2$, the heat of formation under standard state conditions of a 0.3 *M* pertechnic solution then becomes

$$2\mathrm{Tc(c)} + \mathrm{H_2O(l)} + 7/2\mathrm{O_2(g)} + \mathrm{aq.} = 2\mathrm{HTcO_4}(0.3\ M)$$
$$\Delta H^\circ = -278.3 \pm 2.8 \text{ kcal.} \qquad (2)$$

The Heat of Solution of Technetium Heptoxide.—The heat of solution of technetium heptoxide measured on two samples weighing 215.6 and 182.0 mg. was found to be −11.67 and −11.51 kcal. mole^{-1}, respectively. The average value, −11.59 ± 0.08 kcal. mole^{-1}, corresponds to the heat of solution to give an average concentration of 0.041 *M* of pertechnic acid. Assuming that the heat involved in going from 0.041 *M* to infinite dilution is negligible

$$\mathrm{Tc_2O_7(c)} + \mathrm{H_2O(l)} + \mathrm{aq.} = 2\mathrm{HTcO_4,\ aq.}$$
$$\Delta H = -11.59 \pm 0.08 \text{ kcal.} \qquad (3)$$

The Heat of Dilution of a Pertechnic Acid Solution.—Since the solution of pertechnic acid formed in the combustion bomb experiments was still fairly concentrated (0.3 *M*) it was necessary to determine the heat of dilution of this solution to essentially infinite dilution. Two ml. of this pertechnic acid solution was sealed in a small glass bulb and broken in the calorimeter containing 30.00 ml. of water. The heat change corresponded to the *absorption* of 0.28 kcal. mole^{-1} of acid. Neglecting, as before, the heat of dilution of the resulting 0.0205 *M* solution to infinite dilution then 0.28 kcal. mole^{-1} is the heat of dilution of the "bomb" solution to infinite dilution. Combining this with eq. 2 and 3

$$2\mathrm{Tc(c)} + 7/2\mathrm{O_2(g)} + \mathrm{H_2O(l)} + \mathrm{aq.} = 2\mathrm{HTcO_4,\ aq.}$$
$$\Delta H^\circ = -277.7 \pm 2.8 \text{ kcal.} \qquad (4)$$

and

$$2\mathrm{Tc(c)} + 7/2\mathrm{O_2(g)} = \mathrm{Tc_2O_7(c)}$$
$$\Delta H^\circ = -266.1 \pm 2.6 \text{ kcal.} \qquad (5)$$

With the value of −68,317.1 cal. mole^{-1} for the heat of formation of water[27] under standard conditions at 25°, the heat of formation of aqueous pertechnic acid from its elements is −173.0 ± 1.7 kcal. mole^{-1}.

Oxidation–Reduction Potentials.—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,[28] and recently Hugus[29] has 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

$$\text{(acid)} \quad \mathrm{TcO_2} + 2\mathrm{H_2O} = \mathrm{TcO_4^-} + 4\mathrm{H^+} + 3e^- \qquad (6)$$
$$\text{(base)} \quad \mathrm{TcO_2} + 4\mathrm{OH^-} = \mathrm{TcO_4^-} + 2\mathrm{H_2O} + 3e^- \qquad (7)$$

Using the measured potential of the basic cell, the voltage of the acid cell was calculated. This calculated voltage was in good agreement with experimentally determined values.

The acid cell can be represented as

$$\mathrm{Ag/AgCl}\ \Big|\ \mathrm{HCl}\ \Big\vdots\ \begin{matrix}\mathrm{KNO_3}\\ \mathrm{KCl}\end{matrix}\ \Big\|\ \mathrm{HTcO_4}(m)\ \Big|\ \mathrm{TcO_2/Pt} \qquad (8)$$

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

$$3\mathrm{Ag} + 3\mathrm{HCl} + \mathrm{HTcO_4} = 3\mathrm{AgCl} + 2\mathrm{H_2O} + \mathrm{TcO_2} \qquad (9)$$

for which

$$E = E^\circ + \frac{0.0591}{n} \log a^3_{\mathrm{HCl}}\, a_{\mathrm{HTcO_4}} \qquad (10)$$

Since the hydrochloric acid concentration was kept constant (0.05 *M*), the product of the activity coefficient[30] (0.8304) times the concentration can be substituted for the activity of the hydrochloric acid. Substituting numerical values

$$E = E^\circ - 0.1634 + 0.0394 \log m_{\mathrm{HTcO_4}} +$$
$$0.0394 \log \gamma_{\mathrm{HTcO_4}} \qquad (11)$$

TABLE II

E.M.F. OF THE TECHNETIUM DIOXIDE–PERTECHNETATE ELECTRODE IN PERTECHNIC ACID SOLUTIONS

Electrode (+)	E_{obs}, v.	M[31]	$-\log M$	$-0.0394 \log M$	E_1,[32] v.
TcO$_2$ (from zinc reduction)	0.276	0.00135	2.870	0.1131	0.552
	.269	.000679	3.168	.1248	.557
	.251	.000338	3.471	.1380	.552
	.231	.000135	3.870	.1520	.546
			Average	0.552 ± 0.003	
TcO$_2$ (electrolytic)	.268	.00179	2.747	.1082	.540
	.256	.000897	3.047	.1201	.549
			Average	0.545 ± 0.005	
			Total average	0.549 ± 0.004	

If it is further assumed that the activity coefficient of the pertechnic acid in very dilute solutions can be considered as[33]

$$\log \gamma_{\mathrm{HTcO_4}} = -0.5065 M^{1/2} \qquad (12)$$

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

$$E_1 \equiv E + 0.1634 - 0.0394 \log M_{\mathrm{HTcO_4}} =$$
$$E^\circ - 0.01997 M^{1/2} \qquad (13)$$

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[26] F. D. Rossini and M. Frandsen, *J. Research Natl. Bur. Standards*, **9**, 733 (1932).

[27] U. S. Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," 1949.

[28] A. D. Wadsley and H. Walkley, *J. Electrochem. Soc.*, **95**, 11 (1949).

[29] Z. Hugus, as given by Latimer in "Oxidation Potentials," Second Edition, Prentice-Hall, Inc., New York, N. Y., 1952, p. 243.

[30] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, p. 547.

[31] In mole liter^{-1} of pertechnic acid.

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

[33] H. S. Harned and B. B. Owen, ref. 30, p. 119.

When the left side of eq. 13 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° for cell reaction, eq. 9, is obtained.

Calculations using eq. 13 are given in Table II. At concentrations above 0.00135 *M*, small deviations from the limiting behavior were 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 in Table II will be equal to E° since the last term in eq. 13 is negligible at the concentrations given in Table II. From Table II, E_1 is equal to 0.549 ± 0.004 v. E° for the total cell reaction is the sum of E° for the TcO_2–TcO_4^- couple and E° for the Ag–AgCl couple. Using the value for E° of the Ag–AgCl electrode as −0.222 v.,[34] the voltage for the half-cell of eq. 6 becomes −0.771 v. neglecting the effects of junction potentials.

The basic cell may be represented as

$$\mathrm{Hg/HgO}\left|\ \mathrm{NaOH}\ \right\|\begin{array}{c}\mathrm{KCl}\\ \mathrm{KNO_3}\end{array}\left\|\begin{array}{c}\mathrm{NaTcO_4}\\ \mathrm{NaOH}\end{array}\right|\mathrm{TcO_2/Pt} \qquad (14)$$

The cell reaction may be written

$$2NaTcO_4 + 3Hg + H_2O = 3HgO + 2TcO_2 + 2NaOH \qquad (15)$$

and the expression for the voltage at equal concentrations of sodium hydroxide and sodium pertechnetate is

$$E_B = E_B^\circ - \frac{(2)(0.0591)}{3} \log \frac{\gamma_{NaOH}}{\gamma_{NaTcO_4}} \qquad (16)$$

It can be seen that in very dilute solutions, where the activity coefficients of all 1:1 electrolytes are about the same, the measured voltage should correspond to the E_B° for the cell reaction (eq. 15).

Using the average value of 0.409 ± 0.004 v. (see Table III) for the cell reaction and subtracting 0.098 v. for the mercury–mercuric oxide electrode[35] the voltage for half-cell reaction, eq. 7, becomes 0.311 v.

TABLE III

E.M.F. OF THE TECHNETIUM DIOXIDE–PERTECHNETATE ELECTRODE IN BASIC SOLUTION

TcO_2 electrode^{36} (−)	Concentration, *M*	Voltage^{37}
I	0.0683 $NaTcO_4$ .0683 NaOH	0.413 ± 0.003
II	.0683 $NaTcO_4$ .0683 NaOH	.406 ± .005
	Average	.409 ± .004

The two half-cells now can be compared as a test of the assumptions involved in calculating the E° for the acid and basic cells. To convert from the basic to acid cell voltages, $\Delta E = E_B^\circ - E_A^\circ = 1.103$ v. Therefore $E_{B(\text{calcd.})}^\circ = 1.103 - 0.771 = +0.332$ v. The mean averages for both of these half-cells are $\bar{E}_B^\circ = 0.322 \pm 0.011$ v., and $\bar{E}_A = -0.782 \pm 0.011$ v.

Calculations

With the data from previous sections it is now possible to calculate a number of the thermochemical functions. This involves estimation of the appropriate entropy values which can usually be done, using the methods given by Latimer[38] and recently by Cobble,[39] within the accuracy of the experimental measurements. To be consistent, thermochemical information has been taken from the Bureau of Standards compilation,[27] except as otherwise indicated. For calculational purposes the thermochemical quantities have been given to more significant figures than the data justify. For the most part, the errors are of the order of a few per cent.

Pertechnetate Ion (TcO_4^- aq.).—Estimating the entropy of TcO_4^- aq.,[39] as 46.0 cal. mole^{-1} deg.$^{-1}$, and of Tc(c)[40] as 7.4 cal. mole^{-1} deg.$^{-1}$, the entropy of formation becomes −75.0 cal. mole^{-1} deg.$^{-1}$. With ΔH_f° as −173,000 cal. mole^{-1}, ΔF_f° becomes −150,630 cal. mole^{-1}. The potential for the Tc–TcO_4^- couple is then calculated to be −0.472 v.

Potassium Pertechnetate.—Parker[41] has determined the solubility of potassium pertechnetate, and from his data the calculated solubility at 25° is 0.63 mole liter^{-1}. From the activity coefficient of $NaClO_4$ ($\gamma_\pm = 0.60$) at this concentration we estimate[38] $\gamma_\pm$ for $KTcO_4$ to be 0.57; the K_{sp} then becomes 0.129. From the observed temperature coefficient of solubility (ΔH = 9550 cal. mole^{-1}) and the calculated free energy of solution (1220 cal. mole^{-1}) the entropy of solution is 28.0 cal. mole^{-1} deg.$^{-1}$. Using 24.5 cal. mole^{-1} deg.$^{-1}$ for the entropy of K^+ aq., and 46.0 cal. mole^{-1} deg.$^{-1}$ for the pertechnetate ion, the entropy of $KTcO_4$(c) becomes 42.5 cal. mole^{-1} deg.$^{-1}$. The value estimated[38] directly from $KClO_4$(c) by the equation $S_1^\circ - S_2^\circ = 3/2R \ln$ [at. wt. (1)/at. wt. (2)] is 38 cal. mole^{-1} deg.$^{-1}$. The former value was used to calculate the free energy of formation of $KTcO_4$(c). Neglecting any heat of dilution of saturated potassium pertechnetate solutions, and assuming that the heat of neutralization of $HTcO_4$ aq., by KOH aq., is that of a strong acid–strong base (−13,310 cal. mole^{-1} of H_2O formed), the calculated ΔH_f° for $KTcO_4$(c) becomes −242,540 cal. mole^{-1}. Since ΔS_f° is −78.1 cal. mole^{-1} deg.$^{-1}$, then ΔF_f° = −219,250 cal. mole^{-1}. The entropies of other solid pertechnetates can be estimated from the entropy of $KTcO_4$(c) by considering[38] K^+(c) to be 9.2 cal. mole^{-1} deg.$^{-1}$ and assuming that the contribution of TcO_4^-(c) is 33.3 cal. mole^{-1} deg.$^{-1}$; considering $S_{H^+(c)}^\circ = 0$, the entropy of $HTcO_4$(c) is 33.3 cal. mole^{-1} deg.$^{-1}$. This quantity is necessary in order to estimate the entropy of Tc_2O_7(c) from its known hydration entropy.

Technetium Heptoxide (Tc_2O_7(c)).—The entropy of Tc_2O_7(c) may be estimated by the additivity

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[34] H. S. Harned and R. W. Ehlers, THIS JOURNAL, **54**, 1350 (1932).

[35] D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publ. Corp., New York, N. Y., 1939, p. 254.

[36] Electrolytic deposit on platinum.

[37] Against the Hg/HgO electrode.

[38] W. M. Latimer, "Oxidation Potentials," 2nd ed., Prentice-Hall, Inc., New York, N. Y., 1952.

[39] J. W. Cobble, *J. Chem. Phys.*, **21**, 1443 (1953).

[40] J. W. Cobble, to be submitted for publication.

[41] G. W. Parker, Oak Ridge National Laboratory Report ORNL-1116 (1951).

rule[38] or from the entropy given above for $HTcO_4(c)$ and the experimental entropy of dehydration[4]

$$1/2Tc_2O_7(c) + 1/2H_2O(l) = HTcO_4(c) \qquad \Delta S = 2.0 \text{ cal. mole}^{-1} \text{ deg.}^{-1} \tag{17}$$

The value calculated by the former method is 43.9 cal. mole^{-1} deg.$^{-1}$ and from the latter, 45.8 cal. mole^{-1} deg.$^{-1}$. ΔS_f°, using the latter value, is -140.9 cal. mole^{-1} deg.$^{-1}$. Since $\Delta H_f^\circ = -266{,}100$ cal. mole^{-1} according to eq. 5, then $\Delta F_f^\circ = -224{,}080$ cal. mole^{-1} at 25° for $Tc_2O_7(c)$. The corresponding values for $Tc_2O_7(g)$ can be calculated from ref. 4.

Pertechnic Acid ($HTcO_4(c)$).—From the heat of hydration measurements of technetium heptoxide,[4] $\Delta H = -215 \pm 25$ cal. mole^{-1} for equation 17. Therefore $\Delta H_f^\circ = -167{,}420$ cal. mole^{-1} for $HTcO_4(c)$. Since the entropy of $HTcO_4(c)$ is 33.3 cal. mole^{-1} deg.$^{-1}$ as given above, then $\Delta S_f^\circ = -87.7$ cal. deg.$^{-1}$ mole^{-1}, and $\Delta F_f^\circ = -141{,}270$ cal. mole^{-1} for this compound.

Technetium Dioxide ($TcO_2(c)$).—From the potential of the TcO_2–TcO_4^- couple of -0.782 v., and ΔF_f° (TcO_4^-, aq.) as $-150{,}630$ cal. mole^{-1}, ΔF_f° ($TcO_2(c)$) becomes $-91{,}350$ cal. mole^{-1}. Using 14.9 cal. mole^{-1} deg.$^{-1}$ for the entropy of $TcO_2(c)$, estimated by the additivity method, $\Delta S_f^\circ = -41.5$ cal. mole^{-1} deg.$^{-1}$ and $\Delta H_f^\circ = -103{,}720$ cal. mole^{-1} for $TcO_2(c)$ at 25°. The potential of the Tc–TcO_2 couple as calculated directly from the Tc–TcO_4^- couple (-0.472 v.) and the TcO_2–TcO_4^- couple (-0.782 v.) is -0.240 v.

Technetium Trioxide ($TcO_3(c)$).—Using the known difference in heat content of $ReO_3(c)$ and $Re_2O_7(c)$[18] the heat of formation of $TcO_3(c)$ has been estimated from that of $Tc_2O_7(c)$ as $-129{,}000$ cal. mole^{-1}. Using this value, which should be correct within a few per cent., with the estimated value for the entropy as 17.3 cal. mole^{-1} deg.$^{-1}$, $\Delta S_f^\circ = -63.1$ cal. mole^{-1} deg.$^{-1}$ and $\Delta F_f^\circ = -110{,}190$ cal. mole^{-1}. The negative value calculated for the free energy of the following reaction is consistent then with the observation that the trioxide reacts readily in water to disproportionate into the dioxide and pertechnic acid

$$3TcO_3(c) + H_2O(l) + \text{aq.} = 2HTcO_4,\text{ aq.} + TcO_2(c) \qquad \Delta F^\circ = -5 \text{ kcal.} \tag{18}$$

The strengths of Tc–O bonds calculated from the heats of formation of $Tc_2O_7(c)$, $TcO_3(c)$ and $TcO_2(c)$ are 19.0, 21.5 and 25.9 kcal., respectively.

Gaseous Technetium (Tc(g)).—The translational entropy of gaseous technetium can be calculated for the monatomic species as 39.69 cal. mole^{-1} deg.$^{-1}$ at 25° using the Sackur–Tetrode equation.[42] From the spectral observations of Meggers[43] and his assignment of the energy levels (ground state: $^6S_{5/2}$) the electronic contribution is an additional 3.56 cal. mole^{-1} deg.$^{-1}$. The total entropy is thus 43.26 ± 0.01 cal. mole^{-1} deg.$^{-1}$ (omitting nuclear spin). The other energy levels are too far above the ground state (2572.0 cm.$^{-1}$) to contribute to the entropy at room temperatures. Meggers gives the ionization potential as 7.45 v.

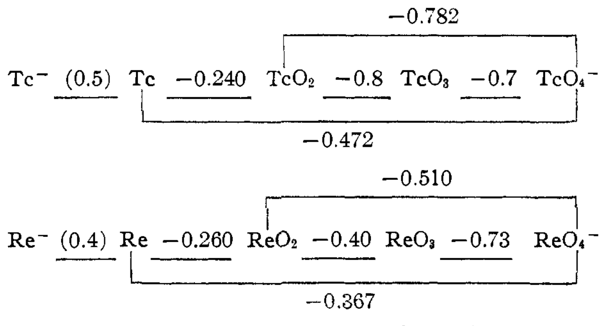

Fig. 3.—Oxidation–reduction scheme for technetium and rhenium in acid solutions.

Oxidation–Reduction Potentials

The oxidation–reduction scheme is given in Fig. 3 and in general resembles that for rhenium.[19] The principal difference lies in the stability of ReO_3 and the instability of TcO_3 with respect to disproportionation. In this respect, technetium (VI) resembles manganese(VI). The value for Tc–Tc^{-1} has been estimated from the value estimated for Re–Re^{-1} given by Latimer,[38] on the assumption that the former is even more unstable (if it exists at all). The reliability of the voltage values are, in general, indicated by the number of significant figures given.

The necessary thermochemical data have been determined to allow a calculation of an oxidation–reduction scheme for technetium. In general this element closely resembles rhenium in its various oxidation states, although technetium (VI) is unstable like manganese(VI). The close resemblance of technetium to rhenium is due, of course, to the similarity of the atoms.[44] This similarity should be expected as a result of the lanthanide contraction.

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[42] K. K. Kelley, Bureau of Mines, Bulletin 477, 1950, p. 9.

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

[44] R. C. L. Mooney, *Phys. Rev.*, **72**, 1269 (1949); *Acta Cryst.* [1], 161 (1948).