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Thermodynamic Properties of Technetium and Rhenium Compounds. III. Heats of Formation of Rhenium Heptoxide and Trioxide, and a Revised Potential Diagram for Rhenium[1]

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Elemental rhenium and rhenium trioxide have been burned in a semimicro bomb calorimeter to redetermine the heats of formation of $Re_2O_7(c)$ and $ReO_3(c)$. These were -295.9 ± 2.0 and -146.0 ± 3.0 kcal. mole^{-1}, respectively. The latter value is in disagreement with that previously reported, but is now consistent with the observed stability of the compound in the presence of water. Using experimental and estimated entropy values, and the recently published potential for the ReO_2–ReO_4^- couple, revised thermodynamic functions are given for rhenium and for some of its compounds. The oxidation-reduction scheme shown in Fig. 1 for the element in acid solution is proposed.

Heats of combustion of elemental rhenium and of rhenium trioxide were determined incidental to other measurements of the thermochemical properties of technetium compounds.[3] Previously, heat values for both of these rhenium substances have been reported by Roth and Becker.[4] However, more accurate data for rhenium trioxide seemed desirable to establish the relative stability of rhenium(VI), which was in doubt, as well as to afford a possible guide for an estimation of the stability of the corresponding technetium compound. Using the new data obtained in this work, a revised potential diagram for rhenium was formulated which appears to be in better agreement with the known chemistry of this element.

Experimental

Materials and Apparatus.—A semi-micro combustion calorimeter already described[3] was employed in the heat measurements. Rhenium metal, prepared by hydrogen reduction of ammonium perrhenate at 500°, was obtained from the University of Tennessee rhenium project. This metal appeared to burn much more completely than that used in the experiments of Roth and Becker which had been formed by reduction of potassium perrhenate; hence, the interpretation of the heats observed by us was not complicated by the necessity to correct for incomplete combustion. To achieve >99% combustion, however, an oil accelerator was required. The heat equivalent of the latter was determined quite accurately in several independent calorimeter experiments. Very small amounts of metallic rhenium which occasionally remained in the semi-micro bomb were weighed to obtain a corrected combustion weight.

Rhenium trioxide, also obtained from the University of Tennessee, had been collected as a by-product from numerous previous burnings of rhenium to give rhenium heptoxide. The trioxide did not burn completely even when an oil accelerator was used, so that corrections for the weights of unreacted compound left in the bomb were necessary. In the calculations one calorie was taken as equal to 4.1840 absolute joules, while 186.31 was employed as the atomic weight of rhenium.

Experimental Results

Calorimetric data for the combustion of rhenium and rhenium trioxide are given in Table I. For rhenium the process measured was

$$2Re(c) + 7/2O_2(g, 30\ atm.) + H_2O(l) = 2HReO_4(\bar{M}) \quad (1)$$

and for rhenium trioxide

$$2ReO_3(c) + 1/2O_2(g, 30\ atm.) + H_2O(l) = 2HReO_4(\bar{M}) \quad (2)$$

where $\bar{M}$ represents the average concentration of the perrhenic acid solution formed with the water in the combustion bomb. Actually, only about one-half of the rhenium heptoxide formed dissolved to give a 0.1 M perrhenic acid solution while the rest remained in the ignition cup. The largest errors, accordingly, arose from the uncertainty about the concentration distribution of perrhenic acid inside the bomb after the combustion.

TABLE I

HEAT DATA FOR RHENIUM AND RHENIUM TRIOXIDE

$\Delta T_{cor.}$,[a] deg.	ΔT_{oil}, deg.	ΔT_{net}, deg.	Sample wt., mg.	Temp. rise, deg. g.$^{-1}$
Rhenium metal				
0.6514	0.5775	0.0739	129.09	0.573
.4464	.3895	.0569	98.77	.576
.6167	.5532	.0635	111.00	.572
			Average[b]	0.574 ± 0.001
$\Delta E = -298.6 \pm 0.4$ kcal. mole^{-1} of Re_2O_7				
Rhenium trioxide				
0.9220	0.9196	0.0024	253.1	0.0095
1.1391	1.1309	.0082	253.7	.0323
0.6198	0.6190	.0008	78.3	.0103
			Average[b]	0.0174 ± 0.008
$\Delta E = -11.4 \pm 6.0$ kcal. mole^{-1} of Re_2O_7				

[a] Corrected for fuse and ignition energy and nitric acid formation. [b] Standard deviations calculated using the relation $S = \Sigma(\Delta X)^2/n(n - 1)$.

Correcting to unit fugacity of oxygen, and the observed energies to enthalpies, we obtain

$$2Re(c) + 7/2O_2(g) + H_2O(l) = 2HReO_4(\bar{M}) \quad (3)$$
$$\Delta H = -300.9 \pm 0.4\ kcal.$$

and, using the data of Roth and Becker[4] to estimate the heat of solution of rhenium heptoxide to give 0.1 M perrhenic acid solutions

$$2Re(c) + 7/2O_2(g) = Re_2O_7(c) \quad (4)$$
$$\Delta H = -295.9 \pm 2.0\ kcal.$$

Because of the modest level of accuracy in the rhenium and rhenium trioxide combustions the Washburn[5] corrections were not applied. The value of -295.9 ± 2.0 kcal. mole^{-1} for the heat of

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[1] This work was performed for the Atomic Energy Commission.

[2] From the Thesis of J. W. C. submitted to the Graduate School of the University of Tennessee in partial fulfillment of the requirements for the Ph.D. degree in June, 1952.

[3] J. W. Cobble, W. T. Smith, Jr., and G. E. Boyd, THIS JOURNAL, **75**, 5777 (1953); paper II of this sequence.

[4] W. A. Roth and G. Becker, *Z. physik. Chem.*, **A159**, 27 (1932); data have been recalculated and summarized in Bureau of Standards "Selected Values of Chemical Thermodynamic Properties," 1948.

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

formation of rhenium heptoxide may be compared with the value, −297.5 ± 2.0 kcal. mole^{-1}, of Roth and Becker.[4] The adoption of the average, −296,700 ± 800 cal. mole^{-1}, is recommended.

Calculations

Perrhenate Ion (ReO_4^-, aq).—Using −13.2 kcal. mole^{-1} for the heat of solution of rhenium heptoxide,[4] the heat of formation of $HReO_4$, aq, becomes −189.2 ± 0.8 kcal. mole^{-1}. Since perrhenic acid is a strong acid, this is also the heat of formation of ReO_4^-, aq. Using −74.2 cal. mole^{-1} deg.$^{-1}$ for the entropy of formation,[6] ΔF_f° becomes −167.1 ± 0.8 kcal. mole^{-1}. The calculated potential for the Re–ReO_4^- couple then becomes $E^\circ = -0.367$ v.

Rhenium Heptoxide ($Re_2O_7(c)$).—The entropy of $Re_2O_7(c)$ can be estimated in three different ways: (a) by the additivity principle:[7] 48.6 cal. mole^{-1} deg.$^{-1}$; (b) by comparison to $Tc_2O_7(c)$[3] correcting for mass differences

$$S^\circ(Re_2O_7) = S^\circ(Tc_2O_7) + 3/2R \ln \frac{\text{at. wt. } Re_2O_7}{\text{at. wt. } Tc_2O_7} \quad (5)$$

which gives 44.9 cal. mole^{-1} deg.$^{-1}$ when the value 43.6 cal. mole^{-1} deg.$^{-1}$ is used for $Tc_2O_7(c)$; (c) from the entropy of $KReO_4(c)$ and the entropy of dehydration of $HReO_4(c)$. The entropy[6] of $KReO_4(c)$ is 40.12 cal. deg.$^{-1}$ mole^{-1} and since 9.2 is the contribution of $K^+(c)$,[7] $ReO_4^-(c)$ becomes 30.9 cal. deg.$^{-1}$ mole^{-1}. The entropy of $HReO_4(c)$ is estimated to be 30.9 e.u. Smith, *et al.*,[8] have measured the entropy of dehydration of perrhenic acid

$$HReO_4(c) = 1/2H_2O(l) + 1/2Re_2O_7(c)$$
$$\Delta S = -3.2 \text{ cal. mole}^{-1} \text{ deg.}^{-1} \quad (6)$$

Thus the entropy calculated by this method for $Re_2O_7(c)$ is 38.6 e.u. Using the average of the three values, 44.0 ± 3.6 cal. mole^{-1} deg.$^{-1}$, ΔF_f° is calculated to be −258.7 kcal. mole^{-1}.

Potassium Perrhenate ($KReO_4(c)$).—With the value for the heat of formation of $HReO_4$ aq, of −189.2 kcal. mole^{-1}, and the heat of solution[3] of $KReO_4(c)$ of 13.8 kcal. mole^{-1}, ΔH_f° ($KReO_4$ (c)) is calculated to be −263.0 kcal. mole^{-1}. This figure is based on the assumption that the heat of neutralization of $HReO_4$ aq, by KOH aq, is that of any strong acid–strong base reaction (−13,310 cal. mole^{-1} H_2O formed). From the experimental values of the entropy of $KReO_4(c)$[6] of 40.12 cal. deg.$^{-1}$ mole^{-1} and the entropy of Re(c)[9] of 8.89 cal. deg.$^{-1}$ mole^{-1}, ΔS_f° becomes −82.0 cal. deg.$^{-1}$ mole^{-1}, and ΔF_f° equals −238.5 kcal. mole^{-1}.

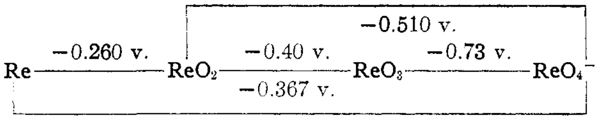

Fig. 1.—Oxidation–reduction scheme for rhenium in acid solution.

Rhenium Trioxide ($ReO_3(c)$).—Correcting the heats given in Table I for $ReO_3(c)$ to unit oxygen fugacity gives

$$2ReO_3(c) + 1/2O_2(g) = Re_2O_7(c)$$
$$\Delta H = -6 \pm 6 \text{ kcal. mole}^{-1} \text{ of } ReO_3 \quad (7)$$

The errors are large in this case due to the uncertainty of corrections for the incomplete combustion of the oxide. The calculated heat of formation of the trioxide then is $\Delta H_f^\circ = -146.0 \pm 3.0$ kcal. mole^{-1}. Roth and Becker[4] reported −83.0 kcal. mole^{-1}. The poor agreement is probably due to the fact that their calculation was based upon the heats observed when rhenium was burned to form a mixture of the heptoxide and varying amounts (4–8%) of the trioxide. The direct determination reported here should be more accurate.

The estimated value of ΔS_f° is −61.5 e.u. for $ReO_3(c)$ based on an estimated[7] entropy of 19.8 e.u. and the experimental value[9] of 8.89 e.u. for the entropy of rhenium. Thus $\Delta F_f^\circ = -127.3$ kcal. mole^{-1}.

Rhenium Dioxide ($ReO_2(c)$).—Latimer[7] reports that Hugus has obtained −0.510 v. for the ReO_2–ReO_4^- couple. Thus the free energy of formation for $ReO_2(c)$ based on this voltage and the free energy of formation given above for ReO_4^-, aq, becomes −89.2 kcal. mole^{-1}. Estimating the entropy of $ReO_2(c)$ as 17.4 cal. mole^{-1} deg.$^{-1}$, $\Delta S_f^\circ = -40.5$ cal. mole^{-1} deg.$^{-1}$ and $\Delta H_f^\circ = -101.3$ kcal. mole^{-1}.

Oxidation–Reduction Potentials

From the above free energies of formation, the potential diagram (Fig. 1) for rhenium in acid solution has been calculated. The reliability of the voltage values is, in general, indicated by the number of significant figures given. The voltages of the ReO_3–ReO_4^- and ReO_2–ReO_3 couples are now in agreement with the observed stability of $ReO_3(c)$ toward disproportionation in acid media. In this respect, $ReO_3(c)$ differs from $TcO_3(c)$, which appears to disproportionate.

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(6) J. W. Cobble, G. D. Oliver and Wm. T. Smith, Jr., This Journal, **75**, 5786 (1953), paper V of this sequence.

(7) W. M. Latimer, "Oxidation Potentials," 2nd ed., Prentice-Hall, Inc., New York, N. Y., 1952.

(8) W. T. Smith, Jr., L. E. Line and W. A. Bell, This Journal, **74**, 4964 (1952).

(9) W. T. Smith, Jr., G. D. Oliver and J. W. Cobble, *ibid.*, **75**, 5785 (1953), paper IV of this sequence.