increased counterion binding also reduces the polyion charge, and hence promotes further diminution of the polyion transport number. On the other hand, the polyion mobility increases markedly with salt concentration. This effect is attributed to the shrinkage of the polymer coil in solutions of high ionic strength.

Although the presence of neutral salt increases the extent of counterion binding, the association of zinc ions with partially neutralized polyacids remains small, although gelation takes place in medium concentration ranges. The experimental data are shown in Fig. 3, indicating association comparable with that shown by sodium ions.[2] This surprisingly small interaction may be due to ion hydration, which could prevent a close approach of zinc ions to any carboxylate group. If the ions have to be dehydrated before association can take place, energetic considerations may explain the observed behavior. In spite of this weak interaction, precipitation took place whenever the low neutralization range was exceeded, presumably because zinc ions can attach themselves to several carboxylate groups, resulting in the formation of polymer clusters. A similar effect was observed with strontium ions, especially in the presence of neutral salt.

URBANA, ILLINOIS

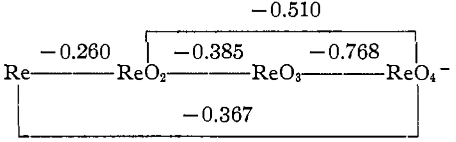
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Thermodynamic Properties of Technetium and Rhenium Compounds. VI. The Potential of the ReO_3/ReO_4^- Electrode and the Thermodynamics of Rhenium Trioxide[1,2]

BY J. P. KING AND J. W. COBBLE

RECEIVED OCTOBER 2, 1956

The potential of the ReO_3/ReO_4^- electrode has been measured over a wide range of concentration and *p*H and the standard electrode potential for the half reaction $ReO_3 + H_2O = ReO_4^- + 2H^+ + e^-$ has been found to be -0.768 ± 0.005 volt. The cell was demonstrated to be satisfactorily reversible by the close agreement of the standard potential calculated from measurements in both acidic and basic solutions, as well as from the reasonable entropy values obtained from a determination of the temperature coefficient. The thermodynamic functions for ReO_3(c) were found to be -146.1 ± 0.8 kcal. mole^{-1}, -128.1 ± 0.8 kcal. mole^{-1} and 19.3 ± 2.5 cal. mole^{-1} deg.$^{-1}$ for the heat of formation, free energy of formation and the entropy, respectively. The revised potential diagram for rhenium in acid solutions becomes



Introduction

In continuation of our general program to characterize the compounds of technetium and rhenium the potential of the rhenium trioxide–perrhenate half-cell has been determined. These data are of importance because of the discordant results previously obtained for the heat of formation of ReO_3(c)[3,4] by combustion calorimetry. Further, direct potential measurements establish more accurately the trend toward disproportionation of ReO_3. Finally, collection of data on reversible oxide electrodes is in itself of interest because of the obviously more complicated nature of the electrode process. Thus reversible potentials have been reported for the MnO_2/MnO_4^-,[5] TcO_2/TcO_4^-[6] ReO_2/ReO_4^-,[7] Hg/HgO,[8] Bi_2O_3/Bi_2O_4,[9] Sb/Sb_2O_3[10] and As/As_2O_3[11] electrode systems. Elucidation of some of the factors which influence reversible electrodes will be the subject of a further communication.

Experimental

Chemicals.—Rhenium heptoxide, used as a starting material in the preparation of rhenium trioxide, was obtained from the University of Tennessee. Purification and dehydration were carried out by vacuum sublimation. This sublimate was dissolved in distilled water to prepare perrhenic acid solutions or transferred by resublimation into various reaction vessels.

Rhenium trioxide was prepared by two reportedly dependable methods involving reduction of rhenium heptoxide by carbon monoxide[12] and dioxane[12,13] at moderate temperatures. It has been our experience that the material produced by the heating of the Re_2O_7–dioxane complex is frequently much darker in color than the normally bright red trioxide obtained from the direct reduction of Re_2O_7 by carbon monoxide. Supposedly the darker color indicates the

---

[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18(600)-1525.

[2] For the preceding paper of this sequence see J. W. Cobble, G. D. Oliver and Wm. T. Smith, Jr., THIS JOURNAL, **75**, 5786 (1953).

[3] W. A. Roth and G. Becker, *Z. physik. Chem.*, **A159**, 27 (1932); see also "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D. C., 1948.

[4] G. E. Boyd, J. W. Cobble and Wm. T. Smith, Jr., THIS JOURNAL, **75**, 5783 (1953).

[5] L. V. Andrews and D. J. Brown, *ibid.*, **57**, 254 (1935).

[6] J. W. Cobble, Wm. T. Smith, Jr., and G. E. Boyd, *ibid.*, **75**, 5777 (1953).

[7] Z. Z. Hugus as reported by W. M. Latimer, "Oxidation-Potentials," Prentice-Hall, New York, N. Y., 1952, p. 243.

[8] F. Fried, *Z. physik. Chem.*, **123A**, 406 (1926); Y. Kobayashi and H. L. Wang, *J. Sci. Hiroshima Univ.*, **5A**, 71 (1934).

[9] E. Baur and W. Lattmann, *Z. Elektrochem.*, **40**, 582 (1934).

[10] R. Schuhmann, THIS JOURNAL, **46**, 52 (1924).

[11] Ref. 7, p. 1444.

[12] L. F. Audrieth, "Inorganic Syntheses," Vol. 3, McGraw-Hill Book Co., New York, N. Y., 1950, pp. 186, 187.

[13] H. Nechamkin, A. N. Kurtz and C. F. Hiskey, THIS JOURNAL, **73**, 2828 (1951).

presence of the lower, black, rhenium dioxide. Both analysis and potentiometric data confirmed this.[14]

Initially the ReO_3 electrodes were prepared by attempting to paste a ReO_3–H_2O slurry onto platinum gauze which was then dried at 50–80°. Electrodes so prepared rapidly disintegrated when immersed in solutions. Attempts to "glue" the ReO_3 onto the gauze with an agar-agar suspension followed by drying gave electrodes so easily polarized as to be unsatisfactory, presumably due to poor electrical contact. Satisfactory electrodes were finally prepared by either subliming Re_2O_7 onto platinum gauze or foil followed by direct reduction with carbon monoxide or, in one case, spreading Re_2O_7–dioxane complex onto platinum gauze and heating to form ReO_3. It is with these electrodes that the cell potentials reported have been obtained.

Reagents which were used were all of reagent grade quality and all solutions were prepared from distilled water. Hydrogen, nitrogen and carbon monoxide gases were obtained from pure grade tank sources; the electrolytic hydrogen was passed through a "Deoxo" catalytic purifier to remove traces of oxygen.

Apparatus.—The acid cell was constructed from a 1" by 4" test-tube fitted with a three-hole stopper. Through this stopper extended the platinum–rhenium trioxide electrode, one end of a salt-bridge, and a small glass tube through which nitrogen gas was bubbled to prevent any possible effects of oxygen on the system.

The platinum–ReO_3 electrode was constructed from a small platinum gauze welded to a platinum wire which was sealed in and through a glass tube. Mercury in the tube provided an electrical contact between the electrode and measuring circuit.

The salt bridge was constructed from very small asbestos fibers sealed through two ends of a U-shaped glass tubing, which was also provided with a stoppered opening for filling. The bridge solution consisted of a 1.8 *M* KNO_3 and 1.8 *M* KCl solution as recommended by Grove-Rasmussen.[15] These procedures were used to prevent excessive flow of bridge solution into the cell, to eliminate the use of organic material in the system which might have reduced ReO_3 and to reduce the possibility of large (and unknown) junction potentials. The other half of the cell was a standard hydrogen electrode, constructed from platinized platinum,[16] and checked against a silver–silver chloride electrode[17] and standardized hydrochloric acid solutions.[18] It appeared to be accurate to at least a millivolt.

The basic cell was constructed from the same ReO_3 half-cell but the reference electrode in this case was a commercial saturated calomel electrode. This electrode was used after unsatisfactory results were obtained with a hydrogen electrode in very high *p*H solutions.

The acid cell solutions were made up by dilution of a concentrated and standardized perrhenic acid solution. The standardization was carried out by a *p*H-potentiometric titration against standard base. In the case of the very dilute solutions, the concentrations were rechecked after the potential measurements by further titration. The basic cell solutions contained sodium perrhenate prepared *in situ* by addition of known amounts of standardized sodium hydroxide solutions. Addition of further sodium hydroxide then brought the *p*H of the solution to the desired value as determined by a direct *p*H determination of aliquots from the solution.

The cells were suspended in a 25.00 ± 0.05° thermostat. Voltages were read on a type K-2 Leeds and Northrup potentiometer which was standardized before each reading against a standard saturated Eppley cell, calibrated by the U. S. Bureau of Standards.

Most of the cells appeared to give reproducible and reversible potentials almost as soon as temperature equilibrium was attained. However, at ReO_4^- concentrations below approximately 0.0005 *f*, and at *p*H values below 9 in the basic cell, sluggishness, drift and loss of precision were apparent so as to make those particular measurements of doubtful value. These values are not included for consideration.

Experimental Results

Acid Cell.—The acid cell may be represented as

$$H_2/Pt\ \left|\ \begin{matrix}HClO_4\\(m_1)\end{matrix}\ \right\|\ \begin{matrix}KCl\\KNO_3\end{matrix}\ \left\|\ \begin{matrix}HReO_4\\(m_2)\end{matrix}\ \right|\ ReO_3(c)/Pt$$

Originally it was assumed that perchloric and perrhenic acids were probably similar enough so that their activity coefficients even at moderate concentrations would be very similar. This was subsequently shown not to be quite correct (see below). However, for purposes of discussion the activities at any concentration of the two acids will be assumed equal; any deviations will be removed when the voltages are extrapolated to infinite dilution.

Under these conditions the following cell reaction can be written

$$^1/_2H_2(g) + HReO_4(aq) = ReO_3(c) + H_2O \qquad (1)$$

Further

$$E = E^0 + 0.0591 \log a_2 \qquad (2)$$

There are various techniques which can be used to test the validity of assuming that the measured voltages correspond to (1) and (2). Since the activity coefficients of perrhenic acid are unknown, then merely changing the *concentration* of the acid does not, in itself, prove the validity of (1). Perhaps the most stringent test is to measure the potentials of the cell in both acid and basic solutions, extrapolate to infinite dilution to obtain both E^0 and $E^0{}_B$ values, checking to see if the differences so obtained correspond to the calculated value of

$$E^0 - E^0{}_B = 0.0591 \log (10^{-14})^2 = -1.655 \text{ volts} \qquad (3)$$

In terms of concentrations, equation 2 becomes

$$E = E^0 + 0.1182 \log m_2\gamma_2 \qquad (4)$$

If it is further assumed that γ_2 can be approximated by the first term of the Debeye–Hückel equation,[19] (4) reduces to

$$E^1 \equiv E - 0.1182 \log m_2 = E^0 - 0.0599 m_2^{1/2} \qquad (5)$$

This equation provides a method for extrapolation of the cell data given in Table I to infinite dilution by plotting the values of E^1 *vs.* $m_2^{1/2}$.

The acid cell data of Table I were obtained from three different ReO_3 electrodes prepared as previously indicated, and identified according to the method of production. In this series of experiments the perrhenic and perchloric acid concentrations were equal.

The values of E' in Table I appear to change with concentration somewhat more than expected, al-

---

[14] The potential of the ReO_2/ReO_4^- electrode is lower (−0.510 volt) than the value reported here for the ReO_3/ReO_4^- electrode (−0.768 v.). ReO_3 electrodes prepared by the Re_2O_7 dioxane process which were noticeably darker than normal almost always gave lower potentials. However, it has been called to our attention that the *surface* color may not be indicative of the purity of the bulk of the material, and that the very nature of the reduction of Re_2O_7 by CO would tend to occlude unreacted Re_2O_7 (or perhaps even lower oxides) in the interior. Excess Re_2O_7 would in all probability be washed out by leaching in water. Further, the electrode reaction does take place on the surface of the material. In the final analysis, of course, one is never sure of the composition of the material undergoing the electrode reaction except that it obeys the Nernst relationship and that the potentials are directly comparable to other thermochemical data, where the composition of the bulk material is again of prime importance.

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

[16] E. Müller, "A Laboratory Manual of Electrochemistry," G. Routledge and Sons, Ltd., London, 1931, p. 19.

[17] Prepared by reducing silver oxide on platinum followed by electrolytic deposition of AgCl as given in H. S. Harned, This Journal, **51**, 416 (1929).

[18] H. S. Harned and R. W. Ehlers, *ibid.*, **54**, 1350 (1932).

[19] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 1st ed., Reinhold Publ. Corp., New York, N. Y., 1943, p. 119.

though the plot of E' *vs.* $m_2^{1/2}$ was linear. The extrapolated value of E' becomes equal to E^0 at infinite dilution and appears to have a value of 0.771 ± 0.002 volt. This value contains uncertainties to the effects of junction potentials and the nonequivalence of $HClO_4$ and $HReO_4$. However, these effects should be greatly reduced by the extrapolation to zero ionic strength, although they are undoubtedly responsible for the change of E' with concentration in Table I. It was not possible to make measurements at lower concentrations because of the unsteady nature of the voltage readings. The accuracy of the cell potentials (± 0.002 volt) is not great enough to evaluate activity coefficients of the ReO_4^- ion, hence no attempt is made to separate the drift of E' values in Table I into the separate activity effects of the two half-cells. Separate ionic strength studies indicated, however, that the activity coefficients of $HReO_4$ appeared to be somewhat lower than those of $HClO_4$ in the ionic strength range listed in Table I. It thus appears that our choice of $HClO_4$ as the electrolyte for the hydrogen electrode was not particularly fortunate.

TABLE I

E.M.F. VALUES FOR THE ReO_3/ReO_4^- ELECTRODE AGAINST THE HYDROGEN ELECTRODE AT 25°

ReO_3 electrode (+)	Eobsd.	m_2	$E'^{(a)}$	$m_2^{1/2}$
C. R.[b] I	0.494	0.0478	0.650	0.216
	.501	.0290	.683	.170
	.500	.0540	.650	.232
C. R. II	.492	.0270	.677	.166
	.487	.0135	.708	.116
	.468	.00680	.724	.082
	.400	.001060	.751	.033
D. R.[c] I	.373	.00054	.760	.023
			.771	0 (extrapolated)

[a] $E' \equiv E_{obsd} - 0.1182 \log m_2$. [b] Electrode material prepared by reduction of Re_2O_7 with CO on platinum. [c] Electrode material prepared by heating Re_2O_7–dioxane complex on platinum.

Basic Cell.—The basic cell consisted of the electrode system

$$Pt/ReO_3 \left| \begin{matrix} NaReO_4(m_3) \\ NaOH(m_4) \end{matrix} \right\| \begin{matrix} KCl \\ (satd.) \end{matrix} \left\| \begin{matrix} KCl\ (satd.) \\ Hg_2Cl_2 \\ (satd.) \end{matrix} \right/ Hg$$

for which the cell reaction

$$2ReO_3 + Hg_2Cl_2 + 4OH^- = 2Hg + 2Cl^- + 2ReO_4^- + 2H_2O \quad (6)$$

can be written. In this case the voltage of the calomel half-cell remained fixed at 0.2415 volt[20] during the concentration study at the basic ReO_3/ReO_4^- electrode; hence

$$E_2{}^{(1/2)} \equiv E_{obs.} - 0.2415 \quad (7)$$

for the half reaction

$$ReO_3 + 2OH^- = ReO_4^- + H_2O + e^- \quad (8)$$

$E_2^{1/2}$ can be expressed as

$$E_2{}^{(1/2)} \equiv E^0_B{}^{(1/2)} - 0.0591 \log a_3/a_4 \quad (9)$$

As in the case of the acid cell, this can be expanded to

$$E_B{}^{1/2} \equiv E_2{}^{1/2} + 0.1182 \log m_{(3)} - 0.2364 \log m_{(4)} = E^0_B{}^{(1/2)} - 0.0599\ \mu^{1/2} \quad (10)$$

where the proper substitutions for the Debye–Hückel relationship[19] have been made. As before, a plot of $E_B{}^{1/2}$ against $\mu^{1/2}$ should lead to the correct value of $E^0_B{}^{(1/2)}$ when extrapolated to infinite dilution. Also as in the case of the acid cell, it was not possible to go to the lowest $[ReO_4^-]$ concentrations (below about 0.003 *f*). The cell did not appear to respond satisfactorily when buffered near the neutral point. The basic cell data are listed in Table II, and lead to a $E^0_B{}^{(1/2)}$ of 0.890 ± 0.008 volt for the half-reaction (8).

TABLE II

E.M.F. VALUES FOR THE ReO_3/ReO_4^- ELECTRODE *vs.* SATD. CALOMEL AT 25° IN BASIC SOLUTIONS

ReO_3 elect. (CR II) sign	E_{obs}	$E_2{}^{1/2}$	m_{NaReO_4}	m_{NaOH}	$E_B{}^{1/2}$	$\mu^{1/2}$
+	0.3280	0.0875	0.0250	2.00×10^{-4}	0.774	0.159
+	.2738	.0323	.0125	4.47×10^{-5}	.838	.112
−	.2107	− .0308	.00625	1.41×10^{-5}	.857	.0798
−	.1600	− .0815	.00312	5.0×10^{-6}	.874	.0562
					.890	0(extrap.)

Temperature Coefficients.—Temperature coefficient studies were made on certain acid cells. Since the observed coefficients were rather small, three different electrodes were used to confirm the results. No attempt was made to do a complete ionic strength study of the temperature coefficient since the unsteady readings at the very lowest concentrations introduce very large errors in the absolute *differences* of the measured voltages, and at the higher ionic strengths the heats of dilution corrections are almost certainly appreciable. Table III contains a summary of the data obtained from four separate runs at 25 and 35°.

TABLE III

TEMPERATURE COEFFICIENT MEASUREMENTS OF THE ReO_3/ReO_4^- ELECTRODE *vs.* THE HYDROGEN ELECTRODE IN ACIDIC SOLUTIONS

ReO_3 electrode (+)	$HClO_4$–$HReO_4$ concn., m	Eobsd. v.	$-E^0$calcd. v.	Temp., °C.	$(dE/dT)_{25}{}^{(a)}$, v./deg.
C R I	0.0478	0.4940	0.6633	25	
		.4771	.6521	35	0.0112 v./deg.
C R I	.0290	.5010	.6934	25	.0136
		.4812	.6798	35	
C R II	.0474	.4990	.6683	25	.0132
		.4800	.6551	35	
C R II	.0502	.4721	.6389	25	.0113
		.4552	.6276	35	
					Av. 0.0121 ± 0.0011

[a] The difference between (dE/dT) at 25 and 30° has been neglected.

Thermochemical Calculations

Standard Electrode Potential.—From the measurements on the acidic cell, the standard potential for the hypothetically ideal one molal solutions of the cell reaction in equation 1 is 0.771 ± 0.002

---

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

volt. Since E^0 for the hydrogen half-cell is zero, then E^0 for the half reaction

$$\mathrm{ReO_3 + H_2O = ReO_4^- + 2H^+ + e^-} \qquad (11)$$

is −0.771 volt. From the measurements in basic solutions, E^0_B for the complementary half-reaction is 0.890 ± 0.008 volt. This value can be converted to the acid E^0 by subtraction of 1.655 volts (equation 3). Thus E^0 from this source for the half cell in (11) is calculated to be −0.765 ± 0.008 volt. The average value, from both acid and basic cells, −0.768 ± 0.005 volt, will be adopted. The confirmatory check between acid and basic cells covering a *p*H range from ∼1.5 to 10.3 is gratifying, and leads one to believe that the electrode is satisfactorily reversible and that the errors arising from junction potentials on the extrapolated potentials are negligible. The corresponding free energy for the half reaction (equation 11) becomes 17,670 ± 120 cal.

The Entropy of $\mathrm{ReO_3(c)}$.—The observed temperature coefficient of the cell reaction (1) of 0.0121 ± 0.0011 volt deg.$^{-1}$ corresponds to a ΔS^0 for the reaction of 27.9 ± 2.5 e.u. Using the experimental[21] value of 48.3 e.u. for the entropy of the perrhenate ion, the entropy of $\mathrm{ReO_3(c)}$ at 25° becomes[22] 19.3 ± 2.5 e.u. This value may be compared to a previous estimate[23] obtained from the additivity principle of 19.8 e.u.; the close agreement is fortuitous, but nevertheless confirms the general reversibility and over all thermodynamic correctness of the cells.

The entropy of formation of $\mathrm{ReO_3(c)}$ from its elements becomes[22] −63.1 ± 2.5 e.u. using the experimental value[24] of 8.89 e.u. for the entropy of elemental rhenium.

Thermodynamic Functions for $\mathrm{ReO_3(c)}$.—The free energy of the half reaction in (11) of 17,670 ± 120 cal. given above can be combined[22] with the experimental value[21] for the free energy of formation of the perrhenate ion of −167, 100 ± 800 cal. mole^{-1} to give −128,100 ± 800 cal. mole^{-1} for the free energy of formation of the trioxide. The heat of formation follows similarly from the entropy of formation given above of −63.1 ± 2.5 e.u. and is calculated to be −146,100 ± 800 cal. mole^{-1}. This may be compared with the two previously discordant values of −83,000[3] and −146,000 ± 3,000[4] cal. mole^{-1} and seems to verify the less accurate thermal data of the latter. Such agreement is again further substantiation of the reversibility of the electrode system. It should be noted, however, that a determination of the low temperature heat capacity and entropy of $\mathrm{ReO_3(c)}$ will lead to a much more accurate entropy of formation for this substance than can be obtained from temperature coefficients studies on these cells.

Revised Potential Diagram.—The revised potential diagram for rhenium in acid solutions is given in Fig. 1 and essentially confirms the stability of $\mathrm{ReO_3}$ toward disproportionation as previously reported.[22]

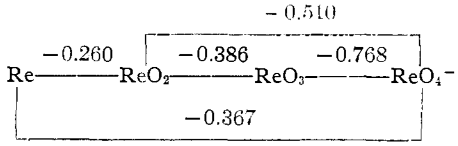


Fig. 1.—Oxidation-reduction scheme for rhenium in acid solution.

The Stability of Rhenate.—It is of some interest to speculate concerning the stability of the rhenate ion, $\mathrm{ReO_4^=}$ in aqueous media. This ion would be the product of the solution of $\mathrm{ReO_3}$ in acid or basic media (assuming $\mathrm{H_2ReO_4}$ to be a moderately strong acid).

The existence of the ion is determined by two factors: stability toward disproportionation and stability toward precipitation

$$\mathrm{4H^+ + 3ReO_4^= = ReO_2 + 2ReO_4^-}$$

$$K_{12} = \frac{[\mathrm{ReO_4^-}]^2}{[\mathrm{H^+}]^4[\mathrm{ReO_4^=}]_3} \qquad (12)$$

$$\mathrm{2H^+ + ReO_4^= = ReO_3 + H_2O}$$

$$K_{13} = \frac{1}{[\mathrm{H^+}]_2[\mathrm{ReO_4}]} \qquad (13)$$

An estimate for both of these constants can be obtained from a prediction of the heat of solution of $\mathrm{ReO_3}$ (the reverse of equation 13.) It appears that the corresponding heat quantities for acid anhydrides in the transition elements range between −8 and +7 kcal. mole^{-1} of aqueous ion. This information is summarized in Table IV.

TABLE IV

HEAT OF REACTIONS OF SOME TRANSITION METAL OXIDES IN WATER AT 25°

Oxide	Ion formed	ΔH[a]
$\mathrm{CrO_3}$	$\mathrm{CrO_4^=}$	+0.3 kcal. mole^{-1} $\mathrm{CrO_4^=}$
$\mathrm{MoO_3}$	$\mathrm{MoO_4^=}$	−5.7 kcal. mole^{-1} $\mathrm{MoO_4^=}$
$\mathrm{WO_3}$	$\mathrm{WO_4^=}$	+2.5 kcal. mole^{-1} $\mathrm{WO_4^=}$
$\mathrm{V_2O_5}$	$\mathrm{V_3O_9^≡}$	−8 kcal. $^1/_3$ mole $\mathrm{V_3O_9^≡}$
$\mathrm{As_2O_5}$	$\mathrm{AsO_4^≡}$	+6.6 kcal. mole $\mathrm{AsO_4^≡}$

[a] Data taken or calculated from reference 20.

Assuming that the heat of solution of $\mathrm{ReO_3}$ to give rhenate will lie between these limits, ΔH_{13} becomes approximately equal to 0 ± 8 kcal. mole^{-1}. If the entropy of $\mathrm{ReO_4^=}$ is 15 e.u.,[25] then ΔF for equation 13 becomes −6 ± 8 kcal mole^{-1}. With these assumptions $(\mathrm{H^+})^2(\mathrm{ReO_4^=}) \approx 5 \times 10^{-5}$, and a solution of rhenate of about 0.1 molal should be stable toward precipitation of $\mathrm{ReO_3}$ at *p*H values greater than 2–3. In basic media, of course, the ion is more stable toward precipitation.

The estimated value of −6 ± 8 kcal. for equation 13 defines a free energy of formation for the rhenate ion of approximately −179 ± 8 kcal. mole^{-1}. Thus ΔF for reaction 12 becomes 214 ± 8 kcal. and the ion is exceedingly stable toward disproportionation. In basic media this stability is increased even further. It would thus seem feasible to prepare moderate concentrations of the rhenate ion and study the $\mathrm{ReO_4^=/ReO_4^-}$ potential directly.

---

[21] J. W. Cobble, G. D. Oliver and Wm. T. Smith, Jr., THIS JOURNAL, **75**, 5786 (1953).

[22] Auxiliary data taken from "Selected Values of Chemical Thermodynamic Properties," U. S. Bureau of Standards, 1949.

[23] G. E. Boyd, J. W. Cobble and Wm. T. Smith, Jr., THIS JOURNAL, **75**, 5783 (1953).

[24] Wm. T. Smith, Jr., G. D. Oliver and J. W. Cobble, *ibid.*, **75**, 5785 (1953).

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

Such studies are being undertaken in our laboratory.

The situation for corresponding technetium compounds is somewhat different. The lower stability of the pertechnetate ion causes TcO_3 to be unstable with respect to disproportionation in acid media, but the technitate ion, $TcO_4^=$ should be stable enough in basic media and even in very dilute acids to allow cell measurements to be made.

Acknowledgment.—The authors are indebted to Mr. Jonathan McPherson for his assistance in certain phases of the work.

LAFAYETTE, INDIANA

[DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Heats of Formation of AmO_2^+(aq) and AmO_2^{++}(aq) in 1 *M* $HClO_4$[1]

BY S. R. GUNN[2] AND B. B. CUNNINGHAM

RECEIVED JULY 23, 1956

The heats of reaction of AmO_2^+(aq) and AmO_2^{++}(aq) with Fe^{++}(aq) in 1 *M* $HClO_4$ have been measured to be −72.2 ± 1.0 and −99.1 ± 0.2 kcal., respectively. From these and other thermodynamic data the heats of formation of AmO_2^+(aq) and AmO_2^{++}(aq) are calculated to be −207.7 ± 2.9 and −170.8 ± 2.7 kcal., respectively. The entropy difference $S_{AmO_2^{++}}$(aq) $- S_{AmO_2^+}$(aq) is calculated to be −16 ± 4 e.u., and a self-consistent potential scheme for the various oxidation states of americium is given. A modified microcalorimeter used in the thermal measurements is described. The autoreduction of AmO_2^+ and AmO_2^{++} and the disproportionation of AmO_2^+ have been investigated.

Introduction

The present investigation was undertaken to secure thermodynamic and kinetic data on the aqueous ions of the higher oxidation states of americium. Estimates of the heats and free energies of the reactions

$$Am(c) + 3H^+(aq) = Am^{+3}(aq) + 3/2H_2(g) \quad (1)$$

and

$$Am^{+3}(aq) + H^+(aq) = Am^{+4}(aq) + 1/2H_2(g) \quad (2)$$

have been reported previously.[3,4]

All thermodynamic values calculated in this paper are for 298°K. and all values used in the calculations are taken from the National Bureau of Standards "Selected Values of Chemical Thermodynamic Properties" unless otherwise stated. The activity coefficients of the aqueous americium ions are not known; hence our heats of formation cannot be designated as $\Delta H°$ values, and the potential values are "formal" rather than "standard."

Experimental

Preparation of Americium Solutions.—The americium isotope used in this work was Am^{241}. Final purification was performed by oxidation-fluoride cycles.[5] Solutions of AmO_2^{++} were prepared by electrolytic oxidation in a cell consisting of three compartments separated by 1-cm. Pyrex "F" sintered discs. The anode and cathode were platinum wire spirals with surface areas of 3.0 and 0.3 cm.², respectively. The Am^{+3} in about 2 ml. of either 1 or 6 *M* $HClO_4$ was placed in the anode compartment and $HClO_4$ of the same concentration in the other two compartments. Electrolysis was performed at a current of 0.15 amp. with the cell immersed in an ice-bath; oxidation was 95% complete within 1 hour. For the calorimetric measurements the oxidized solution was then diluted to about 20 ml. with distilled water or dilute $HClO_4$ and used immediately for measurements of the heat of reduction of AmO_2^{++} or else was allowed to undergo autoreduction to AmO_2^+ for heat measurements on this species.

Autoreduction of AmO_2^+ and AmO_2^{++}.—Spectrophotometric observations of the autoreduction of AmO_2^+ and AmO_2^{++} were in reasonable agreement with the data reported by Asprey and Stephanou[6]; the rate laws are

$$-\frac{d(AmO_2^{++})}{dt} = \frac{d(AmO_2^+)}{dt} = 1.1 \times 10^{-5}(Am_{total})\ sec.^{-1} \quad (3)$$

and

$$-\frac{d(AmO_2^+)}{dt} = \frac{d(Am^{+3})}{dt} = 0.55 \times 10^{-5}(Am_{total})\ sec.^{-1} \quad (4)$$

The reduction is apparently effected mainly by hydrogen peroxide produced in the solution by the *alpha* radioactivity. An experiment in which extra hydrogen peroxide was added to a solution of AmO_2^+ showed the reaction to be first order with respect to (H_2O_2), the half-time being about 1 hour. The reaction of H_2O_2 with AmO_2^{++} was complete before spectra could be recorded, about 5 minutes after mixing.

Solutions of AmO_2^+ thus contain an appreciable steady-state concentration of hydrogen peroxide, but solutions of AmO_2^{++} contain very little peroxide. In freshly prepared solutions of AmO_2^+, the rate of autoreduction is initially zero and increases to the limiting value given by eq. 4 as the peroxide increases to its steady-state concentration. In mixed solutions of AmO_2^{++} and AmO_2^+, no AmO_2^+ is reduced to Am^{+3} until essentially all of the AmO_2^{++} has been reduced to AmO_2^+.

The Calorimeter.—A microcalorimeter previously used in this Laboratory[7] was extensively modified for the present work. The heater and thermometer consist of two coils of No. 42 B. and S. gage enameled copper wire of 40 and 25 ohms, respectively, wound bifilarly on a copper spool 0.010 inch thick, 0.56 inch in diameter and 0.65 inch long. The windings are enclosed by a 0.010 inch copper cover. The spool is centrally positioned in the reaction chamber and also

TABLE I

HEAT OF SOLUTION OF Mg IN 1.00 *M* HCl

Sample wt. (mg.)	Heat evolved, cal.	ΔH, kcal.
0.2280	1.039	−111.1
.1294	0.591	−111.4
.2192	1.002	−111.4

---

[1] Abstracted in part from a dissertation submitted to the Graduate Division of the University of California by Stuart R. Gunn in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] University of California Radiation Laboratory, Livermore, California.

[3] H. R. Lohr and B. B. Cunningham, THIS JOURNAL, **73**, 2025 (1951).

[4] L. Eyring, H. R. Lohr and B. B. Cunningham, *ibid.*, **74**, 1186 (1952).

[5] S. E. Stephanou and R. A. Penneman, *ibid.*, **74**, 3701 (1952).

[6] L. B. Asprey and S. E. Stephanou, American Chemical Society, Chicago (1950).

[7] E. F. Westrum, Jr., and L. Eyring, THIS JOURNAL, **74**, 2045 (1952).