applied to all test fluid data. Temperature and volume flow rate measurements were accurate to within 0.3° C. and 0.25%, respectively. The accuracy of density data, necessary to conversion of turbine flowmeter output to mass flows, was better than 0.1%. Finally, data were corrected for heat release due to propellant decomposition within the apparatus. The over-all error assignable to values of heat capacity reported herein is less than 2%. This conclusion is consistent with the comparisons of present data with prior measurements cited in the literature.

The ranges of test conditions were well removed from the critical points of the test fluids. Estimates of the effect of pressure on heat capacity were made on the basis of density data. In both cases, this effect was less than 0.1% of the values reported. Thus, these data well represent a standard state at 1 atm. or the saturation condition.

SAFETY

Hydrazine is a highly toxic material. It can be absorbed through the skin and can cause blindness on very short contact with the eye. Every effort should be made to avoid oral ingestion, breathing, or skin contact. Good ventilation, safety glasses, and rubber gloves are mandatory.

Compounds of the hydrazine family can undergo violent autodecomposition at high temperatures. They decompose readily in the presence of inorganic catalysts and common residues. Clean glassware and/or stainless steel equipment are necessary safety precautions. Excessive heating—i.e., above 150° C.—is to be avoided. Prolonged confinement under pressure and/or in metal containers is not good practice.

Hydrogen peroxide is nontoxic, but a powerful oxidizing agent. Contact with organic materials should be rigidly avoided. Safety glasses and loose protective garments are recommended for handling quantities beyond laboratory scale.

High strength hydrogen peroxide decomposes readily in the presence of foreign materials and at high temperatures. The procedures recommended above for hydrazine should be adhered to.

LITERATURE CITED

(1) Ahlert, R.C., Report No. R-2094, Rocketdyne, A Division of North American Aviation, Inc., Canoga Park, Calif., 1960.

(2) Giguere, P.A., Morissette, B.G., Olmos, A.W., Knop, O., *Can. J. Chem.* **33**, 804–20 (1955).

(3) Hough, E.W., Mason, D.M., Sage, B.H., *J. Am. Chem. Soc.* **72**, 5774–5 (1950).

(4) Jones, R., Report No. S-13731, Shell Development Co., Emeryville, Calif., 1957.

(5) Mueller, K.H., Report No. R-2655, Rocketdyne, A Division of North American Aviation, Inc., Canoga Park, Calif., 1960.

(6) Scott, D.W., Oliver, G.D., Gross, M.E., Hubbard, W.N., Huffman, H.M., *J. Am. Chem. Soc.* **72**, 2293–7 (1949).

RECEIVED for review November 6, 1967. Accepted February 12, 1968. The work on hydrogen peroxide was sponsored by the Bureau of Aeronautics, U. S. Navy, under Contract NOas 56-1052d, and the work of hydrazine was sponsored by the Air Force Flight Test Center, Headquarters Air Research and Development Command, Edwards Air Force Base, Calif., under Contract AF33(616)-6768. This work was also presented as a Master's thesis by Curtis A. Younts at UCLA (Professor T. E. Hicks, Committee Chairman).

Enthalpy of Formation of Cerium Sesquioxide

FLOYD B. BAKER and CHARLES E. HOLLEY, Jr.
University of California, Los Alamos Scientific Laboratory, Los Alamos, N.M. 87544

Oxygen bomb calorimetry was used to determine the energy of combustion of Ce_2O_3. The enthalpy change for the reaction Ce_2O_3-hexagonal + $\frac{1}{2}O_2 = 2CeO_2$ was $\Delta H^\circ_{298.15^\circ K.} = -91.05 \pm 0.16$ kcal., which leads to a value for the enthalpy of formation of Ce_2O_3 of $\Delta H^\circ_{f\,298.15^\circ K.} = -429.31 \pm 0.68$ kcal. per mole.

THE enthalpy of combustion in oxygen of Ce_2O_3 has been measured by Kuznetsov, Rezukhina, and Golubenko (*9*), who found $\Delta H^\circ_{298.15^\circ K.} = -85.43 \pm 0.26$ cal. per mole, and by Mah (*10*) who found $\Delta H^\circ_{298.15^\circ K.} = -93.35 \pm 0.10$ kcal. per mole. The difference is 7.92 kcal. per mole, many times the combined estimated uncertainties of the measurements.

In addition, the reaction $CeO_{2-x} + (x/2)O_2 = CeO_2$ has been studied by measurements of oxygen partial pressures by Kuznetsov *et al.* (*8*), Brauer, Gingerich, and Holtschmidt (*2*), and Bevan and Kordis (*1*) and by electromotive force measurements on cells with solid electrolytes by Kuznetsov *et al.* (*8*) and by Markin and Rand (*11*). These various equilibrium measurements are in reasonable agreement among themselves. Those of Bevan and Kordis (*1*) are perhaps the most complete, and they find, for the oxidation of Ce_2O_3-hexagonal to CeO_2, the value $\Delta H^\circ_{1353^\circ K.} = -93.2 \pm 1.0$ kcal. per mole, which, on conversion to room temperature (*4*) becomes $\Delta H^\circ_{298^\circ K.} = -90.3 \pm 1.0$ kcal. per mole, a value lying intermediate between the two combustion values.

In view of this discrepancy, the enthalpy of combustion of Ce_2O_3-hexagonal was remeasured to obtain a more reliable value for its enthalpy of formation.

EXPERIMENTAL

Cerium nitrate (American Potash and Chemical Corp.) was converted to the oxalate, which was then ignited to CeO_2. The CeO_2 was reduced in a graphite boat under purified H_2 at about 1300° C. for 12 hours. Hydrogen was purified using a model Ch-A Milton Roy Serfoss hydrogen purifier. The preparations with the higher oxygen content were made with less pure hydrogen. Spectrochemical analysis showed the presence of faint traces of silicon and copper. Other impurities were less than the limits of detection. X-ray analysis of preparation 1 showed the presence of the hexagonal form of Ce_2O_3 with lattice parameters $a = 3.892 \pm 0.001$ A. and $c = 6.059 \pm 0.001$A. and small amounts of another phase, presumably a higher oxide. Combustion analysis of each preparation showed H_2 ranging from 0.003 to 0.012% and carbon from 0.005 to 0.010%.

It was necessary to handle the samples in an inert atmosphere box because of a slow reaction with air; however, there was negligible weight gain of samples exposed to the dry oxygen atmosphere in the bomb for 1 hour.

Samples were burned on sintered CeO_2 disks in oxygen at 25 atm. pressure in a bomb calorimeter at an average initial temperature of 25.0° C. Ignition was made by magnesium fuse wire except for two runs in which cerium fuse wire was used to check for any extraneous heat effect from the magnesium. The apparatus and details have been described (*6*).

The calorimeter temperatures were measured to 0.001° C. with a platinum resistance thermometer and a Müller bridge. Times were measured to the nearest second. The corrected temperature rise was determined by the method of Dickinson (*3*) and is believed to be accurate to ±0.001° C. The 2000 grams of water in the calorimeter can was weighed to 0.01 gram. The combustion samples were weighed to 0.0001 gram and the fuse wire to 0.00001 gram. The CeO_2 disks were weighed to 0.1 gram. The precision of the calorimeter as measured by twice the standard deviation of the mean on combustions of benzoic acid is 6 parts in 23,000 or about 0.03%.

The energy equivalent of the calorimeter as determined by combustion of standard benzoic acid (NBS sample 39i) was 2384.3 ± 0.6 cal. per degree, the calorie being the defined thermochemical calorie, equal to exactly 4.184 absolute joules.

Each combustion product was heated in an atmosphere of oxygen to determine if any unburned material remained. In all runs, combustion was essentially 100% complete. The oxygen-to-cerium ratio was also determined by combustion analysis.

RESULTS

Twenty runs were made from five different preparations with varying oxygen-to-cerium ratios. The uncorrected results are given in Table I.

These measured energies of combustion were then corrected for the hydrogen and carbon impurities, which were assumed to be present as the elements, using the following ΔH_f° values: H_2O, −57.8 kcal. per mole; CO_2, −98.9 kcal. per mole. All other impurities were assumed to be present as their oxides. The enthalpies of combustion, reduced to unit fugacity of oxygen and converted to a constant pressure process are given in Table II on a molar basis, assuming the atomic weight of Ce to be 140.12. The value for O-Ce = 1.500 was obtained by extrapolation of a least squares line through the experimental points when plotted against composition.

By combining the enthalpy of combustion of Ce_2O_3 with the enthalpy of formation of CeO_2 (5) one obtains for the enthalpy of formation of Ce_2O_3 $\Delta H^\circ_{f298.15^\circ K.} = -429.31 \pm 0.68$ kcal. per mole. If the carbon impurity was present as cerium carbide, the enthalpy of formation of Ce_2O_3 could

Table I. Energy of Combustion of Ce_2O_y at 25° C.

(Uncorrected for impurities.)

Mass Burned, G.	Wt.[a] Fuse, Mg.	Wt. CeO_2, G.	Energy Equiv., Cal./Deg.	ΔT, ° K.	Firing Energy, Cal.	Energy from Ce_2O_y, Cal./G.	Dev. from Mean, Cal./G.
			Preparation 1				
7.0133	4.34	26.9	2389.4	0.7214	0.4	−242.1	0.3
8.8076	4.91	27.2	2389.4	0.9112	1.7	−243.7	1.3
9.2893	3.68	27.7	2389.5	0.9455	0.8	−240.8	1.6
9.1788	4.10	31.3	2389.7	0.9431	0.4	−242.8	0.4
						Av. −242.4	σ = 1.2
			Preparation 2				
10.9491	3.85	30.8	2389.7	1.1578	0.4	−250.6	0.2
10.0883	5.02	29.0	2389.6	1.0744	1.8	−251.4	1.0
10.2346	4.17	26.6	2389.4	1.0834	1.4	−250.4	0.0
6.9010	3.64	26.6	2389.4	0.7287	1.0	−249.1	1.3
						Av. −250.4	σ = 0.8
			Preparation 3				
11.7698	5.19	27.3	2389.4	1.3475	1.3	−270.8	0.4
9.0079	5.07	27.0	2389.4	1.0367	1.3	−271.5	0.3
9.3601	2.70	26.0	2389.3	1.0693	0.9	−271.2	0.0
9.2273	3.14	26.7	2389.4	1.0556	0.8	−271.2	0.0
						Av. -271.2	σ = 0.3
			Preparation 4				
8.5855	4.14	26.0	2389.3	0.9791	0.4	−269.6	0.0
9.1468	3.54	26.2	2389.3	1.0406	0.5	−269.5	0.1
9.1436	3.83	26.3	2389.3	1.0380	0.4	−268.7	0.9
9.2388	4.73	27.7	2389.4	1.0584	0.7	−270.6	1.0
						Av. −269.6	σ = 0.6
			Preparation 5				
9.0187	3.88	26.5	2389.4	1.0380	1.0	−272.3	0.5
9.2315	4.78	26.7	2389.4	1.0686	0.8	−273.4	0.6
						Av. −272.8	σ = 0.8
			Preparation 5 (Ce fuse wire)				
9.1992	74.82	28.0	2389.5	1.1095	1.6	−273.0	0.5
9.2744	73.46	27.6	2389.5	1.1128	1.4	−272.0	0.5
						Av. −272.5	σ = 0.7

[a] Magnesium fuse wire except the last two runs which used cerium fuse wire.

Table II. Enthalpy of Combustion of Ce_2O_x for Various Oxygen to Cerium Ratios at 25° C.

Prep.	H_2, %	C, %	y	$-\Delta H^\circ_{298.15^\circ K.}$ Kcal./Mole	Std. Dev.[a]
1	0.004	0.010	3.097 ± 0.002	79.86	0.11
2	0.0048	0.005	3.076	82.24	0.080
3	0.012	0.007	3.024	88.22	0.074
4	0.008	0.009	3.024	88.17	0.073
5	0.003	0.006	3.012	89.58	0.088
5	0.003	0.006	3.016	89.40	0.083
Extrapolated[b]			3.000	91.05	0.080

[a] Standard deviation of the mean from the least squares fit of the data. [b] $\Delta H^\circ_{298.15^\circ K.} = (115.61 \pm 1.82)y - (437.88 \pm 2.73)$ kcal. per mole where the uncertainty is the standard deviation.

Table III. Thermodynamic Functions for the Reaction Ce_2O_3-hexagonal + $\frac{1}{2}O_2 = 2CeO_2$

T, ° K.	$-\Delta H^\circ$, Cal.	$-\Delta S^\circ$, Cal./Deg.	$-\Delta G^\circ$, Cal.
100	90,350 ± 160	26.66 ± 0.50	87,680 ± 170
200	90,820 ± 160	30.00 ± 0.50	84,820 ± 190
298.15	91,050 ± 160	30.96 ± 0.50	81,820 ± 220
300	91,050 ± 160	30.96 ± 0.50	81,760 ± 220
400	91,250 ± 170	31.54 ± 0.54	78,630 ± 280
500	91,490 ± 190	32.09 ± 0.62	75,450 ± 360
600	91,750 ± 210	32.55 ± 0.70	72,220 ± 470
700	92,010 ± 240	32.97 ± 0.84	68,930 ± 640
800	92,280 ± 280	33.33 ± 0.92	65,620 ± 790
900	92,560 ± 320	33.7 ± 1.0	62,230 ± 960
1000	92,850 ± 360	34.0 ± 1.1	58,850 ± 1200
1100	93,150 ± 400	34.3 ± 1.2	55,420 ± 1400
1200	93,460 ± 450	34.6 ± 1.2	51,940 ± 1600
1300	93,780 ± 500	34.8 ± 1.3	48,540 ± 1800
1400	94,140 ± 540	35.0 ± 1.3	45,140 ± 1900

$\Delta H^\circ_0 = -88{,}780 \pm 160$ cal.
$\Delta G^\circ = -90{,}230 + 6.02\ T \log T + 13.3\ T$ cal.

Table IV. Thermodynamic Functions for the Formation of Ce_2O_3-hexagonal

T, ° K.	$-\Delta H^\circ_f$, Cal./Mole	$-\Delta S^\circ_f$, Cal./Deg./Mole	$-\Delta G^\circ_f$, Cal./Mole
100	428,010 ± 680	68.16 ± 0.53	421,190 ± 680
200	428,400 ± 680	71.28 ± 0.57	414,140 ± 690
298.15	429,310 ± 680	73.50 ± 0.62	407,400 ± 700
300	429,310 ± 680	73.50 ± 0.62	407,260 ± 710
400	428,730 ± 680	71.86 ± 0.65	399,990 ± 730
500	428,010 ± 690	70.27 ± 0.72	392,870 ± 780
600	427,270 ± 690	68.89 ± 0.79	385,940 ± 840
700	426,550 ± 700	67.79 ± 0.91	379,100 ± 950
800	425,880 ± 710	66.9 ± 1.0	372,400 ± 1100
900	425,260 ± 730	66.2 ± 1.1	365,700 ± 1200
1000	424,690 ± 760	65.4 ± 1.2	359,300 ± 1400
1100	427,990 ± 790	68.7 ± 1.3	352,400 ± 1600
1200	427,420 ± 820	68.2 ± 1.3	345,600 ± 1800
1300	426,820 ± 850	67.7 ± 1.3	338,800 ± 1900
1400	426,140 ± 890	67.2 ± 1.3	332,000 ± 2000

$\Delta H^\circ_0 = -423{,}750 \pm 680$ cal./mole.
$\Delta G^\circ_f = -428{,}920 - 5.85\ T \log T + 87.5\ T$ cal./mole.

be as much as 0.5 kcal. per mole too high, or if oxycarbide, the error would be less than 0.5 kcal. per mole.

DISCUSSION

The value for the enthalpy change of the reaction Ce_2O_3-hexagonal + $\frac{1}{2}O_2 = 2CeO_2$ obtained in this work is thus $\Delta H^\circ_{298.15^\circ K.} = -91.05 \pm 0.16$ kcal. The numerically lower value obtained by Kuznetsov, Rezukhina, and Golubenko (*9*), possibly could have resulted from their Ce_2O_3 having become slightly oxidized. Mah's numerically higher value (*10*) is more difficult to understand. However, the authors noticed that the reduced Ce_2O_3 contained some hydrogen and carbon, as mentioned above, which would have given a numerically higher result if no correction had been made for it.

By the use of the low temperature heat capacity measurements of Westrum and Beale (*16*) and the high temperature enthalpy increment measurements of King and Christensen (*7*) for CeO_2, and similarly the low temperature heat capacity measurements of Weller and King (*15*) and the high temperature enthalpy increment measurements of Pankratz and Kelley (*12*) for Ce_2O_3-hexagonal, the thermodynamic functions for this reaction were calculated as a function of temperature as shown in Table III. [The reader is referred to (*4*) for a discussion of why these measurements were chosen in preference to other available measurements and also for the method used in estimating the uncertainty intervals.] The resulting value for the enthalpy change of the reaction at 1353° K. is $\Delta H^\circ_{1353^\circ K.} = -93.96 \pm 0.52$ kcal., in good agreement with the value -93.2 ± 1.0 kcal. found by Bevan and Kordis (*1*).

Table IV, which gives the thermodynamic functions for the formation of Ce_2O_3-hexagonal as a function of temperature, was calculated in a similar manner, making use of the low temperature heat capacity measurements of Parkinson, Simon, and Spedding (*13*) and the high temperature enthalpy increment measurements of Spedding, McKeown, Daane (*14*) for cerium metal.

ACKNOWLEDGMENT

The authors appreciate the efforts of Finley Ellinger, x-ray analysis, and E. J. Huber for helpful discussion.

LITERATURE CITED

(1) Bevan, D.J.M., Kordis, J., *J. Inorg. Nucl. Chem.* **26**, 1509 (1964).
(2) Brauer, G., Gingerich, K., Holtschmidt, U., *Ibid.*, **16**, 77 (1960).
(3) Dickinson, H.C., *Bull. Bur. Std.* **11**, 189 (1914).
(4) Holley, C.E., Jr., Huber, E.J., Jr., Baker, F.B., "The Enthalpies, Entropies, and Gibbs Energies of Formation of the Rare Earth Oxides," in "Progress in Science and Technology of the Rare Earths," Vol. **3**, LeRoy Eyring, Ed., Macmillan, New York, in press.
(5) Huber, E.J., Jr., Holley, C.E., Jr., *J. Am. Chem. Soc.* **75**, 5645 (1953).
(6) Huber, E.J., Jr., Matthews, C.O., Holley, C.E., Jr., *Ibid.*, **77**, 6493 (1955).
(7) King, E.G., Christensen, A.U., *U. S. Bur. Mines Report Invest.* No. **5789** (1961).
(8) Kuznetsov, F.A., Belyi, V.I., Rezukhina, T.N., Gerasimov, Ya. I., *Dokl. Akad. Nauk SSSR* **139**, 1405 (1961).
(9) Kuznetsov, F.A., Rezukhina, T.N., Golubenko, A.N., *Russ. J. Phys. Chem.* (English Transl.) **34**, 1010 (1960).
(10) Mah, A.D., *U. S. Bur. Mines Rept. Invest.* No. **5676** (1961).
(11) Markin, T.L., Rand, M.H., "Thermodynamics," Vol. 1, p. 145, International Atomic Energy Agency, Vienna, 1966.
(12) Pankratz, L.B., Kelley, K.K., *U. S. Bur. Mines Rept. Invest.* No. **6248** (1963).
(13) Parkinson, D.H., Simon, F.E., Spedding, F.H., *Proc. Roy. Soc. (London)* **A207**, 137 (1951).
(14) Spedding, F.H., McKeown, J.J., Daane, A.H., *J. Phys. Chem.* **64**, 289 (1960).
(15) Weller, W.W., King, E.G., *U. S. Bur. Mines Rept. Invest.* No. **6245** (1963).
(16) Westrum, E.F., Jr., Beale, A.F., Jr., *J. Phys. Chem.* **65**, 353 (1961).

RECEIVED for review November 13, 1967. Accepted February 12, 1968. Work done under the auspices of the U. S. Atomic Energy Commission.