θ_D was found to be approximately 78. With this value of θ_D, and also taking into consideration the temperature dependence of experimental values of C_p at the lowest temperatures (14–20°K.), the increase of entropy from 0 to 14°K. is estimated to be 0.63 e.u. with an uncertainty of ±0.06 e.u. The uncertainties in the entropy calculations, due to errors in the measurements of the heat of vaporization and heat capacity and in the estimation of gas imperfections, are estimated, respectively, to be ±0.03, ±0.04 and ±0.03 e.u. The total uncertainty in the entropy of F_2 is therefore about ±0.16 e.u.

TABLE VIII

THERMODYNAMIC FUNCTIONS OF FLUORINE (F_2)

Temp., °K.	C_p, cal./mole/deg.	S, cal./mole/deg.	$(H - H_0)/T$, cal./mole/deg.	$-(F - H_0)/T$, cal./mole/deg.
		Solid I		
15	1.745	0.741	0.5226	0.218
20	3.104	1.422	0.9915	.431
25	4.609	2.276	1.564	.712
30	6.031	3.245	2.192	1.053
35	7.427	4.281	2.842	1.439
40	8.778	5.363	3.502	1.861
45	10.142	6.475	4.164	2.311
45.55	10.290	6.599	4.237	2.362
		Solid II		
45.55	11.120	10.417	8.055	2.362
50	11.792	11.486	8.359	3.127
53.54	12.210	12.308	8.600	3.708
		Liquid		
53.54	13.700	14.586	10.879	3.708
55	13.698	14.955	10.954	4.001
60	13.680	16.146	11.182	4.964
65	13.607	17.239	11.372	5.867
70	13.558	18.245	11.529	6.716
75	13.642	19.182	11.666	7.516
80	13.793	20.067	11.794	8.273
85	13.948	20.907	11.916	8.991
85.02	13.948	20.909	11.917	8.992
85.02 (Vapor)	....	39.287	30.281	8.996
85.02 (Ideal gas)	....	39.577	.....	...

The entropy of F_2 in the ideal gas state has been calculated at various temperatures from spectroscopic data by Cole, Farber and Elverum,[11] and by Haar and Beckett.[12] Their values of entropy at 85.02°K. are, respectively, 39.62 ± 0.02 and 39.56 ± 0.01 e.u., which are in close agreement with the value obtained from our calorimetric data (39.58 ± 0.16).

Derived Thermodynamic Functions

The heat capacity and the derived thermodynamic functions for F_2 at selected integral values of temperature are given in Table VIII.

[11] L. G. Cole, M. Farber and G. W. Elverum, Jr., *J. Chem. Phys.*, **20**, 586 (1952).

[12] L. Haar and C. W. Beckett, National Bureau of Standards Report 1435 (1952).

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

The Heat of Combustion of Cerium[1]

BY ELMER J. HUBER, JR., AND CHARLES E. HOLLEY, JR.

RECEIVED MAY 14, 1953

A precise measurement has been made of the heat of combustion of cerium metal. It was found to be 7749 ± 10 joules/g. at an oxygen pressure of 25 atm. The heat of formation of CeO_2 at 25° is calculated to be −1088.6 ± 1.4 kjoules/mole. This value differs by 7 to 12% from those found in the literature.

Introduction.—Values in the literature[2-4] for the heat of formation of CeO_2 are in poor agreement, presumably because of the use of impure cerium metal. This paper reports the results of the combustion of analyzed cerium metal to determine the heat of formation of its dioxide.

Method.—The method involved the determination of the heat evolved from the burning of a weighed sample of the metal in an oxygen bomb calorimeter at a known pressure. The energy equivalent of the calorimeter was determined from the heat of combustion of standard benzoic acid and also was determined electrically. The completeness of combustion was determined by treating the combustion products with 6 *N* perchloric acid and measuring the amount of hydrogen evolved from any unburned metal present.

The uncertainties given are twice the standard deviations.

The results are expressed in absolute joules and also in defined calories; 1 defined calorie = 4.1840 absolute joules.

Apparatus.—The details of the construction and calibration of the calorimeter have been described.[5] The energy equivalent of the calorimeter with oxygen at 25 atmospheres pressure was 10,096.6 ± 3.1 joules/deg.

Cerium Metal.—The cerium metal was supplied by Dr. F. H. Spedding of the Ames Laboratory of the A. E. C. This metal was analyzed at the Los Alamos Scientific Laboratory with the following results: Na, 0.05%; Mg, 0.01; Ca, 0.005; La, 0.01; C, 0.0090; N, 0.0975; O, 0.244 and H, < 0.001. Any other metallic impurities were present in amounts too small to be detected by the spectroscopic method used. The metal was thus about 99.57% cerium. The chemical state of the impurities is not known. However, if it is assumed that the oxygen, nitrogen and carbon are combined with cerium as CeO_2, CeN and CeC_2, respectively, and not combined with the metallic impurities, then the material is 97.48 atomic per cent. cerium metal. A Debye X-ray pattern of the metal showed only lines of the metal in the cubical form.

Combustion of Cerium.—The cerium was burned as chunks on sintered discs of cerium dioxide supported on a platinum platform weighing 103.8 g. New discs were used

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[1] This work was done under the auspices of the A. E. C.

[2] W. Muthmann and L. Weiss, *Ann.*, **331**, 1 (1904).

[3] H. Hirsch, *Trans. Electrochem. Soc.*, **20**, 57 (1911).

[4] J. Moose and S. Parr, THIS JOURNAL, **46**, 2656 (1924).

[5] C. E. Holley, Jr., and E. J. Huber, Jr., *ibid.*, **73**, 5577 (1951).

TABLE I

THE HEAT OF COMBUSTION OF CERIUM

In Runs 1 and 7 only 99.98% of the cerium burned.

Run	Mass Ce burned, g.	Wt. CeO_2, g.	Wt. Mg, g.	Joules/deg. total	ΔT, °K.	Energy total	Energy from—				Dev. from mean. j./g.
							Firing, j.	Mg, j.	Ce, j.	Ce, j./g.	
1	1.6223	55.7	0.0072	10132.3	1.2395	12559.0	17.9	177.6	12363.5	7621.0	7.1
2	1.5574	48.3	.0060	10129.5	1.1899	12053.1	21.6	148.0	11883.5	7630.3	2.2
3	1.6609	52.8	.0070	10131.2	1.2693	12859.5	16.3	172.7	12670.5	7628.7	.6
4	1.6906	49.6	.0065	10130.0	1.2899	13066.7	16.3	160.3	12890.1	7624.6	3.5
5	1.6549	53.4	.0051	10131.5	1.2629	12795.1	11.2	125.8	12658.1	7648.9	20.8
6	1.7258	45.4	$.0055_5$	10128.4	1.3134	13302.6	15.1	136.9	13150.6	7620.0	8.1
7	1.5232	47.0	$.0052_5$	10129.0	1.1626	11776.0	7.3	129.5	11639.2	7641.3	13.2
8	1.6669	48.3	.0058	10129.6	1.2702	12866.6	16.6	143.1	12706.9	7623.1	5.0
9	1.7404	46.7	$.0055_5$	10128.8	1.3240	13410.5	11.2	136.9	13262.4	7620.3	7.8
10	1.6749	55.2	$.0044_5$	10132.2	1.2761	12929.7	20.5	109.8	12799.4	7641.9	13.8
11	1.7657	52.9	.0053	10131.2	1.3428	13604.2	15.2	130.7	13458.3	7622.1	6.0
12	1.7028	52.4	.0054	10131.1	1.2945	13114.7	9.3	133.2	12972.2	7618.2	9.9
13	1.5642	52.7	.0056	10131.1	1.1919	12075.3	11.1	138.1	11926.1	7624.4	3.7
									Av. =	7628.1	7.8

for each run. The discs were made by mixing 0.5% dextrin in water with the powder and pressing in a steel die at 10,000 p.s.i. They were fired in air for eight hours at 1150°. No gas was evolved from the discs upon treatment with 6 *N* $HClO_4$. Pure magnesium was used for the fuse wire. Its heat of combustion was taken as 24,667 joules/g.[5] The amount varied from 0.0044 to 0.0074 g. There is no formation of a double oxide from cerium and magnesium oxides.[6] Correction was made for the electrical energy used in igniting the wire. The total energy equivalent of the calorimeter and contents was used, taking into account the discs, the platinum, and the difference in energy equivalent between the cerium oxide formed and the oxygen used. The completeness of combustion varied from 99.98 to 100.00%. The initial temperature was 24.6° and the average final temperature was 25.8°.

The results of 13 runs at 25 atm. pressure may be summarized as follows: mass of cerium used, 1.52 to 1.76 g.; firing energy, 7.3 to 21.6 joules; energy from magnesium fuse wire, 110 to 178 joules; temperature rise, 1.16 to 1.34°; energy from cerium, 7618.2 to 7648.9 joules/g. with an average value of 7628.1 joules/g.; average deviation from the mean, 7.8 joules/g.; standard deviation of the mean, 2.7 joules/g. This average value of 7628.1 ± 5.5 joules/g. must be corrected for the impurities present.

Correction for Impurities.—If it is assumed that the oxygen is present as CeO_2, the nitrogen as CeN which burns to CeO_2 and N_2O_5(s), and the carbon as graphite, the percentage composition of the metal, by weight, is Ce metal, 97.53; CeO_2, 1.31; CeN, 1.07; Na, 0.05; C, 0.01; Mg, 0.01; La, 0.01; Ca, 0.01. The carbon is probably present as CeC_2, but the heat of formation of the latter is not known and is probably small. Since the amount of carbon is small the error thus introduced is small. The metallic impurities are assumed to contribute according to their heats of combustion in the pure state. Heats of alloy formation and heats of solution are ignored. If we let Q be the heat of combustion of pure cerium metal, per gram, then we may write the following equation: $0.9753Q + 0.0107 \times 5040 + 0.0005 \times 18{,}000 + 0.0001 \times 33{,}000 + 0.0001 \times 25{,}000 + 0.0001 \times 6400 + 0.0001 \times 16{,}000 = 7{,}628.1$ where the first term is the heat from the Ce metal, the second term is from the CeN, 5040 being the heat of combustion per gram of CeN to CeO_2 and N_2O_5, the third term is from the Na, the fourth term from the C, the fifth term from the Mg, the sixth term from the La, and the seventh term from the Ca. The sum of these terms is equated to the observed heat of combustion per gram. Solving, $Q = 7748.5$ joules/g.

If an alternative assumption is made that the metallic impurities are present as oxides, with the extra oxygen present as CeO_2, the nitrogen as CeN and the carbon as graphite, then the percentage compositions of the metal by weight is Ce metal, 97.69; CeO_2, 1.12; CeN, 1.07; Na_2O, 0.07; MgO, 0.02; La_2O_3, 0.01; CaO, 0.01; C, 0.01. Setting up the equation for Q again: $0.9769Q + 0.0107 \times 5040 + 0.0001 \times 33{,}000 = 7628.1$. In this equation the first term is the heat from the Ce metal, the second term is from the CeN, and the third term is from the C. Solving, $Q = 7749.8$ joules/g.

The average of these two values is 7749.2 which can be rounded off to 7749 joules/g. The correction due to impurities amounts to 1.6% of the uncorrected value.

Calculation of the Uncertainty.—The uncertainty to be attached to the corrected value includes the uncertainty in the energy equivalent, which is 0.03%, the uncertainty in the calorimetric measurements, which is 5.5 joules/g. or 0.07%, and the uncertainty introduced in the correction for impurities.

The main uncertainty introduced in the correction for the impurities is the accuracy of the analyses. The O, N and C were determined chemically and it is estimated that they are correct to 2%. The Na, Mg, La and Ca were determined spectroscopically and it is estimated that they are correct to 50%. If the amounts of impurities are increased by the above mentioned percentages and Q recalculated, the value 7756.8 joules/g. is obtained. On this basis, then, the uncertainty introduced in the correction is taken as the difference between 7757 and 7749 or 8 joules/g. which is 0.10%. There are additional small uncertainties, not taken account of, which have been discussed in the previous section.

Combining these uncertainties, then, the over-all uncertainty $= \sqrt{0.03^2 + 0.07^2 + 0.10^2} = 0.13\% =$ 10 joules/g. And the final corrected value is 7749

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[6] H. v. Wartenberg and K. Eckhardt, *Z. anorg. allgem. Chem.*, **232**, 179 (1937).

± 10 joules/g. for the heat of combustion of cerium metal in oxygen at 25 atmospheres pressure.

Composition of the Cerium Dioxide.—The cerium oxide formed was brown in color. An X-ray pattern showed only lines of cubical CeO_2.

Heat of Formation of CeO_2.—The heat of combustion reported above gives for the reaction in the bomb a value of $\Delta E_{24°} = -1085.9 \pm 1.4$ kjoules/mole. The correction of this value to 25° is less than the uncertainty in the result. To obtain the heat of formation it is necessary to correct for the deviation of oxygen from the perfect gas law and to convert from ΔE to ΔH. Using Rossini and Frandsen's[7] value of $(\partial\Delta E/\partial P)_{301°K.} = -6.51$ joules/atm./mole for oxygen and, taking $\Delta H = \Delta E + \Delta(PV)$, we have for the heat of formation of CeO_2, $\Delta H_{25°} = -1088.6 \pm 1.4$ kjoules/mole. In defined calories this is -260.18 ± 0.33 kcal./mole. This value differs by about 6.8% from the value of -243.6 kcal./mole obtained by Hirsch[8] which has been accepted by Brewer[8] as being the most reliable. It differs by 11.7% from the value of -233 kcal./mole selected by the National Bureau of Standards,[9] evidently from the work of Moose and Parr.[5]

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They also are very appreciative of the courtesy of Dr. F. H. Spedding of Ames Laboratory, A. E. C., through whom the cerium metal was obtained.

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

[8] L. Brewer, "The Thermodynamics of the Rare Earths," UCRL-1931, Sept., 1952.

[9] "Selected Values of Chemical Thermodynamic Properties," N. B. S. Circular 500, 1952, p. 348.

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[CONTRIBUTION FROM THE U. S. NAVAL RADIOLOGICAL DEFENSE LABORATORY]

Ion Exchange as a Separation Method. VI. Column Studies of the Relative Efficiencies of Various Complexing Agents for the Separation of Lighter Rare Earths

BY S. W. MAYER AND E. C. FREILING

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Using columns of Dowex-50 cation-exchange resin at 87°, Sm–Eu and Eu–Tb separation factors have been determined for a number of complexing agents under dynamic conditions. A comparison of the separation factors thus obtained yields the following order of selectivity for the complexing agents studied: EDTA > lactate = glycolate > malate ≥ citrate. EDTA (ethylenediaminetetraacetate) has the disadvantage of low solubility in the *p*H range most suitable for good separations.

Introduction

Until now, buffered solutions of citric acid have been used almost exclusively in the separation of rare earths by cation-exchange chromatography. Although it has been shown that improved separations are obtained in a given time by the use of elevated temperatures,[1,2] no effects of varying the conditions of the eluting agent at the convenient temperature of 87° have been reported. In attempting to achieve an improved separation of the lighter rare earths in a relatively short period of time, we have made a number of column studies at 87° using Dowex-50 cation-exchange resin. These studies involved (1) variation of the *p*H and concentration of citric acid and (2) extension of the equilibrium studies of Tompkins and Mayer[3] to dynamic conditions and to include other complexing agents. Data have been obtained for the relative efficiencies of citric, lactic,[4] malic, glycolic and ethylenediaminetetraacetic (EDTA) acids.

The results of other investigations have indicated that Eu and Sm offer a convenient pair of difficultly separable rare earths. In our studies, the efficiencies of eluting conditions were determined by comparing the purity of Eu and Sm obtained, as well as that of Y and Tb which likewise are difficult to separate.

We have been primarily interested in seeking column conditions which would give the maximum purification of the lighter rare earths within a reasonable period of time. For this reason, conditions were always chosen in an effort to obtain a residence time of approximately 8 hr. for Sm. Such a procedure required the simultaneous alteration of more than one variable.

Experimental

Materials.—Commercial 250–500 mesh Dowex-50 cation-exchange resin was graded to obtain that portion which settled through 6 in. of water in from 2 to 15 min. This portion was washed with 6 *N* HCl to remove Fe, converted to the ammonium form with concentrated NH_4OH and finally washed with distilled water.

The β-emitting isotopes Sm^{153}, $Eu^{152,154}$, Tb^{160} and Y^{91} were used to trace the elution histories of the various runs.

Eluting agents were prepared with boiled distilled water; toluene was added as a preservative. The *p*H of these solutions was adjusted with C.P. NH_4OH and measured on a Beckman Model G *p*H meter.

Apparatus and Procedure.—The columns were made from thick-walled capillary tubing (1.6 mm. i.d.). A 10-mm. Pyrex tubing, sealed to the upper end of the column, served as a preheating reservoir for the eluting agents. By packing these columns with freshly boiled resin while they were maintained at 87°, bubble formation was almost entirely eliminated as long as the columns were kept hot and the *p*H of the eluting agent was kept below 3.5.

Before beginning a run, each column was preconditioned with the appropriate eluting agent and then washed with about 2 ml. of boiled distilled water. Next active solutions were added and allowed to pass through the column. These were followed immediately by the eluting agent.

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[1] B. H. Ketelle and G. E. Boyd, THIS JOURNAL, **69**, 2800 (1947).

[2] S. G. Thompson, B. B. Cunningham and G. T. Seaborg, *ibid.*, **72**, 2798 (1950).

[3] E. R. Tompkins and S. W. Mayer, *ibid.*, **69**, 2859 (1947).

[4] Before we had completed any of the column runs with lactate solutions, we received a private communication from H. Petrow to the effect that lactate solutions appeared to be more effective than citrate for the praseodymium–neodymium separation on ion-exchange columns operated at room temperature.