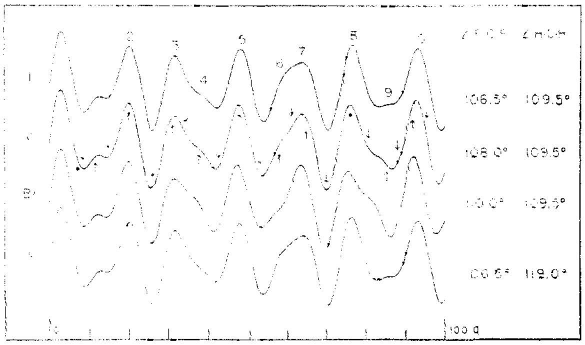

Fig. 1.—Difluoromethane: theoretical intensity curves.

and 6–7, the position of maximum 9, and the relative depths of minima, 5, 6 and 8. Such qualitative considerations and comparisons of the observed and calculated positions of maxima and minima (see Table I for an example close to our final model) lead to the following values of the structural parameters: C–F/C–H = 1.36/1.09 (assumed), C–F = $1.35_7 \pm 0.01_7$ Å., ∠F–C–F = 107.5 ± 1.5°, ∠ H–C–H = 109.5° (assumed), symmetry C_{2v} (assumed). The effect of varying the H–C–H angle is small (compare curves I and L), and any possible error in the assumed value can have no significant effect upon the values of the determined parameters.

TABLE I

COMPARISONS OF OBSERVED AND CALCULATED POSITIONS Maxima and Minima (Curve J)

No.	Minima $q_{\text{obsd.}}$[a]	Minima $q_{\text{calcd.}}/q_{\text{obsd.}}$	Maxima $q_{\text{obsd.}}$	Maxima $q_{\text{calcd.}}/q_{\text{obsd.}}$
1	8.15	(1.067)	11.17	(1.083)
2	15.09	(0.928)	19.95	(0.995)
3	25.94	0.991*	31.02	1.017
4	34.26	1.036	37.69	1.008
5	42.67	0.980	47.84	0.997*
6	52.67	1.020	57.71	1.005
7	61.35	0.978	64.96	0.978
8	70.09	0.999*	76.19	.998*
9	80.46	1.007	85.05	.976
10	87.95	0.984	91.30	1.014
11	95.04	1.036		
Average 17 features		0.9990		
Average deviation		0.014		
Average 4 starred features		0.9963		
Average deviation		0.003		

Best model: C–F = 0.9980 × 1.36 = 1.35_7

[a] Average of W. H. and K.H. measurements.

Our results differ significantly from those of the early electron diffraction study in the value of the F–C–F angle, which we find to be more than 2° smaller. Our photographs, extending to a considerably larger scattering angle, presumably allow a more reliable interpretation of the difficult doublets 3–4 and 6–7 upon which the early angle determination was largely based as well as enabling us to see maximum 9, of which the position and degree of association with adjacent maxima are very F–C–F-angle sensitive. The C–F bond length result from the infrared investigation stands well outside our limit of error. It is to be noted, however, that the preliminary results of a recent microwave investigation[5] (which appeared during the course of our work) C–F = 1.36 Å., C–H = 1.09 Å., ∠ F–C–F = 108°, ∠ H–C–H = 112°, agree well with ours.

Acknowledgment.—We wish to thank Professor Verner Schomaker for his helpful comments regarding the interpretation of some of the more difficult features of the pattern.

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The Heat of Combustion of Neodymium[1]

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Introduction.—Only in recent years have some of the rare earth metals become available in highly purified form. The information available in the literature on the heats of formation of the rare earth oxides is in some cases very meager and in those cases where considerable data are available the agreement between the different investigators is poor. It was therefore thought desirable to make an investigation of the heats of formation of those rare earth oxides for which the metals could be obtained.

This paper reports the results obtained on neodymium metal. The only previous work found by us in the literature on the heat of formation of Nd_2O_3 is that of Muthmann and Weiss[2] who obtained $\Delta H_f = -435$ kcal./mole.

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 25 atmospheres 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* hydrochloric acid and measuring the amount of hydrogen evolved from any unburned metal present.

The uncertainties given are twice the corresponding standard deviations.

Apparatus.—The details of the construction and calibration of the calorimeter have been described.[3] The energy equivalent of the calorimeter was 10,096.6 ± 3.1 joules/°.

Neodymium Metal.—The neodymium metal was supplied by Dr. F. H. Spedding of the Ames Laboratory of the Atomic Energy Commission. This metal was analyzed with the following results: Na, 0.02; Mg, 0.01; C, 0.034; N, 0.06; and O, 0.21. Any other metallic impurities were present in amounts too small to be detected by the spectroscopic method used. An X-ray Debye pattern of the metal showed only lines for the metal. There was no evidence of neodymium hydride.

Combustion of Neodymium.—The neodymium was burned as chunks on sintered discs of 99% pure Nd_2O_3 supported on a platinum platform weighing 103.8 g. A new disc was used for each run. Pure magnesium wire was used. Its heat of combustion was taken as 24,667 joules/g.[3] The amount varied from 0.0087 to 0.0091 g. 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 disc, the platinum and the difference in energy equivalent between the neodymium

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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) C. E. Holley, Jr., and E. J. Huber, Jr., THIS JOURNAL, **73**, 5577 (1951).

oxide formed and the oxygen used up. The completeness of combustion of the neodymium varied from 99.86% to 99.96%. The initial temperature was 24.6° and the average final temperature was 25.8°. The results are summarized in Table I.

TABLE I

COMBUSTION OF NEODYMIUM

Mass Nd, g.	ΔT, °C.	Total energy, abs. joules	Energy from Nd, abs. joules/g.	Deviation abs. joules/g.
2.0327	1.2626	12,782.4	6171.0	0.9
1.8968	1.1790	11,935.5	6171.1	1.0
2.0332	1.2622	12,778.5	6171.4	1.3
2.0242	1.2554	12,709.7	6164.4	5.7
2.0523	1.2744	12,902.2	6172.8	2.7
		Average:	6170.1	2.3

2 × standard deviation = 2.9

The value given in the table for the heat of combustion of neodymium metal as used must be corrected for the impurities present. If it is assumed that the oxygen is present as Nd_2O_3, that the carbon contributes according to the heat of combustion of graphite, and that the other impurities are negligible, the corrected value for the heat of combustion of neodymium is 6252.6 joules/g.

Finally, the uncertainty attached to this value must include, in addition to the ±2.9 joules given in the table, the uncertainty in the energy equivalent. When this is included, the heat of combustion of neodymium is found to be 6252.6 ± 3.5 absolute joules/g.

Composition of the Neodymium Oxide.—The neodymium oxide formed was a very dark blue-black in color. An X-ray Debye pattern showed only lines of hexagonal Nd_2O_3. The possibility that the dark color was due to excess oxygen was investigated by use of the "active oxygen" method of Barthauer and Pearce.[4] The formula of the neodymium oxide was found by this method to be $Nd_2O_{3.001}$.

Heat of Formation of Nd_2O_3.—The heat of combustion reported above gives, for the reaction in the bomb, a value of $\Delta E_{24.6°} = -1804.1 \pm 1.0$ 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[5] value of $(\partial \Delta E/\partial P)_{301°\text{K.}} = -6.51$ joules/atm./mole for oxygen and taking $\Delta H = \Delta E + \Delta(PV)$, we have for the heat of formation of Nd_2O_3, $\Delta H_{25°} = -1808.1 \pm 1.0$ absolute kjoules/mole. In defined calories this is -432.15 ± 0.24 kcal./mole. This value is about 0.7% lower than the value -435 kcal./mole obtained by Muthmann and Weiss.[2]

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[4] G. L. Barthauer and D. W. Pearce, *Ind. Eng. Chem.*, **18**, 479 (1946).

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

Some Properties of Iron Biscyclopentadienyl

BY LOUIS KAPLAN, WILLIAM L. KESTER AND JOSEPH J. KATZ

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Recent reports[1,2] of the preparation of the remarkable new compound, iron biscyclopentadienyl, have led us to investigate the possibility of preparing similar compounds of other transition elements. In the course of this work we have prepared and measured some of the properties of the iron compound. Current interest[3] in the structure of this compound prompts us to publish some of our results.

Iron biscyclopentadienyl was prepared by the addition of one-third of a molar equivalent of ferric chloride to cyclopentadienylmagnesium bromide, both dissolved in tetrahydrofuran. After removal of the solvent, the product was isolated from the residue in 51% yield, based on ferric chloride, by sublimation under reduced pressure. It was purified by repeated sublimation in a high vacuum. The color of the solid, orange at room temperature, was observed to change reversibly to a brilliant

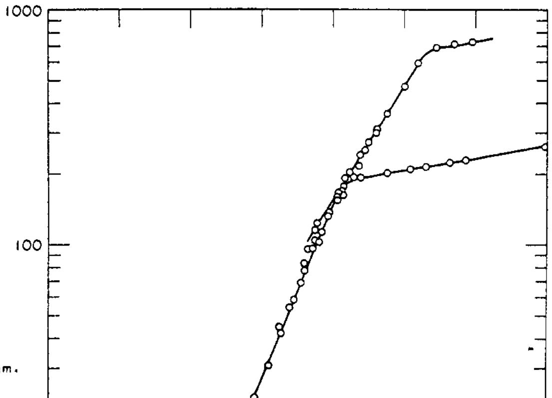

Fig. 1.—Vapor pressure of iron biscyclopentadienyl.

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