The hydrogen azide was admitted in the usual manner. It was then pumped down to a pressure of about 0.02 mm. The trap, J, was packed in ice and readings of the two gages were made. From the value $\Sigma(p\sqrt{M})$ obtained from the fiber gage was subtracted 0.0030 mm. corresponding to the $p\sqrt{M}$ of the mercury vapor present. The remainder, divided by the pressure, as read on the McLeod gage, gave $\sqrt{M}$. The results are given in Table IV.

TABLE IV

MOLECULAR WEIGHT OF GASEOUS HN_3

p (mm. × 10^2) (McLeod)	$\Sigma(p\sqrt{M}) \times 10^2$ (Quartz fiber)	M	Dev. from av.
2.26	15.46	44.9	1.3
2.00	12.90	39.7	3.9
1.47	9.96	43.3	0.3
1.24	8.75	46.5	2.9
		Av. 43.6	2.1

Summary

Gaseous hydrogen azide has been found to be decomposed by ultraviolet radiation from an aluminum spark, giving hydrogen, nitrogen and ammonia (ammonium azide). These products are formed by concurrent reactions; on brief illumination 27% of the decomposition gives H_2 and N_2 and 73% gives NH_3 and N_2.

By means of the quartz fiber and McLeod gages, the molecular weight of hydrogen azide has been determined as 43.6 ± 2.1.

PASADENA, CALIFORNIA

THE SPECIFIC HEATS AT LOW TEMPERATURES OF MANGANOUS OXIDE, MANGANOUS–MANGANIC OXIDE AND MANGANESE DIOXIDE[1]

BY RUSSELL W. MILLAR[2]

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The present article is one of a series from this Laboratory dealing with the thermodynamic properties of the oxides of metals which are important in metallurgical processes. Preceding articles have dealt with zinc oxide,[3] but it is now proposed to extend the investigations to many other oxides, as well as to several sulfides.

The specific heats of the oxides of manganese so far determined have been confined, with the exception of those of Russell[4] at low temperatures,

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Associate Chemist, Pacific Experiment Station, Bureau of Mines.

[3] (a) Maier, THIS JOURNAL, **48**, 356 (1926); (b) Maier and Ralston, *ibid.*, **48**, 364 (1926); (c) Maier, Parks and Anderson, *ibid.*, **48**, 2564 (1926).

[4] Russell, *Physik. Z.*, **13**, 59 (1912).

to the measurements of Regnault[5] and Kopp[6] at slightly above room temperature. The previous results are summarized in Table I.

TABLE I

THE MOLAL HEAT CAPACITY OF MnO AND MnO_2

Substance	t, °C.	C_p	Investigator
MnO	13–98	11.14	Regnault
MnO_2	−187–78.0	8.50	Russell
MnO_2	−78.2–0	12.23	Russell
MnO_2	2.4–48.3	14.27	Russell
MnO_2	17–48	13.8	Kopp

The method of the present investigation was that originally used by Eucken[7] in Nernst's laboratory, and has since been adopted by almost all investigators in this field.

The apparatus differed but little from that of Gibson and Giauque,[8] who improved considerably on the original design. Changes, however, were made, some of which have been described by Giauque, Buffington and Schulze.[9] The vacuum jacket, 10 by 25 cm. in size, was of brass tubing with walls 3 mm. thick. The cover, which was of brass 13 mm. thick, was soldered onto the jacket. The heavy protecting shield was of lead poured between concentric copper tubes. The wall of the outer tube was made 6 mm. thick, in order to distribute rapidly the heat generated in a coil of constantan wire wound in grooves on the outer surface. A copper sheath protected the shield from radiation. The protecting shield, with its cover, weighed 8 kilograms.

The cover of the shield, of 2.5cm. copper sheet, was secured by machine screws. In it were Bakelite conduits through which passed the wires leading to the calorimeter. Each wire, before passing through the cover, was soldered to one end of a strip of thin copper clamped by a screw to the cover but insulated from it by very thin mica. Heat passing down the wire thus found its way to the shield of high heat capacity instead of to the calorimeter.

The calorimeter, of copper tubing 3.7 by 13 cm., was wound with about 260 feet of No. 40 B. & S. gage double silk covered copper wire, which served as both thermometer and heating coil. Additional insulation and thermal contact were obtained with Bakelite varnish. The calorimeter was protected from radiation by a sheath of copper, 0.025 mm. in thickness, which was stuck on by Bakelite varnish. Rapid distribution of heat was obtained by means of sheets of 0.13mm. copper, parallel to each other and to the axis of the calorimeter, which were soldered at their edges to the inner wall. Since these sheets were spaced at 3 mm. and the voids between the particles of the sample were filled with hydrogen, the distribution of heat was so rapid that thermal equilibrium was obtained in three to ten minutes. The volume of the calorimeter was 130 cc., the weight, 115 g.

With respect to the vacuum system and the electrical wiring, the apparatus was similar to that of Gibson and Giauque. Electrical measurements were made with a White double potentiometer and time measurements with an accurately calibrated stop watch.

The copper resistance thermometer was calibrated during the specific heat determinations for each substance by means of a single junction copper–constantan thermocouple soldered to the bottom of the calorimeter. This thermocouple was made of wire

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[5] Regnault, *Ann. chim. phys.*, [3] 1, 129 (1841).

[6] Kopp, *Phil. Trans.*, [1] **155**, 71 (1865).

[7] Eucken, *Physik. Z.*, **10**, 586 (1909).

[8] Gibson and Giauque, THIS JOURNAL, **45**, 93 (1923).

[9] Giauque, Buffington and Schulze, *ibid.*, **49**, 2343 (1927).

from the same spool as thermocouple No. 17 of Giauque, Buffington and Schulze.[9] This thermocouple was compared with No. 17 through a secondary standard, and No. 17 was itself compared by Giauque, Buffington and Schulze with the hydrogen gas thermometer, and with the hydrogen and oxygen vapor pressure thermometers by Giauque, Johnston and Kelley.[10]

The correction for the exchange of heat between the calorimeter and its surroundings was made by the assumption of Newton's law of cooling. The small correction for the difference in temperature between the thermometer wire and the average temperature of the calorimeter described by Giauque and Wiebe[11] was calculated and applied. At room temperature this correction often amounts to as much as 1% and occasionally 2%, but at liquid air temperatures only about 0.1% correction is necessary on this account. The effect of the correction is to lower the calculated value of the specific heat.

Materials.—Manganous–manganic oxide was prepared by igniting a good grade of C. P. manganous sulfate in platinum at 1100°. The sample was heated for a week, pulverized and heated again as before. It was then heated in a current of gaseous hydrochloric acid according to St. Clair-Deville;[12] nitrogen was passed over the hot crystals for three hours to displace the hydrochloric acid, and the product was cooled. The product was finely crystalline. The preparation showed 1.006 times the oxidizing power of pure manganous–manganic oxide toward oxalic acid. Although Meyer and Rötgers[13] state that oxidation of manganous–manganic oxide prepared by the ignition of manganese dioxide does not occur in air, possibly under the conditions of the present test this particular sample combined with the small amount of oxygen in the nitrogen.

Manganous oxide was prepared by reduction of amorphous manganous–manganic oxide by hydrogen and crystallization by gaseous hydrochloric acid. A finely crystalline, bright green product resulted. This product showed no oxidizing power toward oxalic acid but the total manganese determined by oxidation to manganese dioxide with standard potassium permanganate corresponded to only 99.0% manganous oxide. Correction was made in the specific heats for the impurity, which consisted of small flakes of silica from the wall of the preparation flask.

Manganese dioxide was prepared by heating the nitrate at 170° until the evolution of the oxides of nitrogen had ceased. The product was 99.6% manganese dioxide.

The results are given in Tables II–V.

TABLE II

THE HEAT CAPACITY PER GRAM MOLECULE OF MnO

Run no.	T, °K.	C_p	Run no.	T, °K.	C_p	Run no.	T, °K.	C_p	Run no.	T, °K.	C_p	Run no.	T, °K.	C_p
1	70.4	4.426	9	116.5	17.65	17	111.0	10.53	25	116.2	23.96	33	203.3	9.173
2	74.3	4.869	10	118.9	7.530	18	112.0	10.98	26	117.1	7.837	34	217.5	9.462
3	82.1	5.650	11	92.1	6.797	19	113.0	11.71	27	...	....	35	229.7	9.592
4	88.5	6.348	12	96.5	7.362	20	113.9	12.50	28	128.6	7.482	36	247.1	9.728
5	109.1	9.829	13	98.9	7.757	21	114.8	13.78	29	143.3	7.793	37	272.9	9.992
6	118.5	7.564	14	104.8	8.769	22	115.5	23.70	30	155.6	8.124	38	289.1	10.16
7	126.8	7.470	15	108.8	9.664	23	115.7	67.68	31	178.0	8.625	39	293.7	10.26
8	134.5	7.593	16	109.9	10.13	24	115.9	107.56	32	189.7	8.927	40	300.2	10.30

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[10] Giauque, Johnston and Kelley, THIS JOURNAL, **49**, 2367 (1927). The author takes this occasion to express his gratitude to Professor Giauque for his kindness in furnishing him with the temperature scale and for many suggestions during the progress of the measurements.

[11] Giauque and Wiebe, THIS JOURNAL, **50**, 101 (1928).

[12] St. Clair-Deville, *Compt. rend.*, **53**, 199 (1861).

[13] Meyer and Rötgers, *Z. anorg. allgem. Chem.*, **57**, 104 (1908).

TABLE III

THE HEAT ABSORPTION PER MOLE, ΔH, BETWEEN T_1 AND T_2 FOR MnO

Run no.	T_1	T_2	ΔH	Run no.	T_1	T_2	ΔH
9	115.810	117.109	22.93	22	115.152	115.647	11.73
17	110.488	111.533	11.01	23	115.644	115.830	12.61
18	111.538	112.533	10.93	24	115.823	115.942	12.80
19	112.544	113.476	10.91	25	115.943	116.429	11.64
20	113.485	114.357	10.90	27	109.937	121.207	147.17
21	114.315	115.161	10.97				

TABLE IV

THE HEAT CAPACITY PER GRAM MOLECULE OF Mn_3O_4

Run no.	T, °K.	C_p	Run no.	T, °K.	C_p
1	72.2	9.725	14	188.0	26.26
2	76.0	10.46	15	199.1	27.34
3	85.5	12.11	16	200.4	27.37
4	95.6	13.68	17	209.4	28.23
5	103.6	15.02	18	220.0	28.75
6	111.9	16.45	19	233.2	30.15
7	121.5	18.02	20	241.4	30.69
8	129.8	19.25	21	252.5	31.28
9	138.2	20.29	22	263.1	32.07
10	151.9	22.14	23	271.5	32.45
11	160.0	23.08	24	283.4	32.76
12	167.4	23.97	25	295.3	33.35
13	177.6	25.11	26	305.2	33.46

TABLE V

THE HEAT CAPACITY PER GRAM MOLECULE, C_p, OF MnO_2

Run no.	T, °K.	C_p	Run no.	T, °K.	C_p	Run no.	T, °K.	C_p
1	95.6	6.406	14	72.8	3.901	26[a]	...	....
2	97.4	6.193	15	74.8	4.151	27	221.9	11.24
3	107.2	5.847	16	76.7	4.372	28	236.6	11.70
4	90.2	7.262	17	78.8	4.619	29	249.8	12.19
5	115.4	6.285	18	81.1	4.994	30	72.5	3.875
6	119.7	6.514	19	83.4	5.370	31	74.6	4.114
7	130.2	7.006	20	86.0	5.849	32	91.8	8.510
8	139.6	7.494	21	88.3	6.450	33	92.5	9.034
9	148.8	7.996	22	90.3	7.343	34	93.2	8.667
10	166.9	8.869	23	92.9	8.658	35	93.9	7.810
11	179.3	9.453	24	93.7	8.140	36	292.6	13.60
12	188.7	9.872	25	95.4	6.549	37	293.8	13.53
13	199.5	10.35						

[a] Run No. 26. Heat absorption between 87.743 °K. and 98.437 °K. = 76.35 cal./mole.

The figure accompanying this text displays the results for all three oxides. Table III shows the heat input for the points which fall on the steep slopes of the specific heat curve for manganous oxide, and the initial and final temperatures. Obviously the curve rises so rapidly that the recorded heat capacities at the average temperatures are not valid and cannot be plotted; in the figure they are used only to indicate the course of the curve.

No reason can be given for the discontinuities in the curves for manganous oxide and manganese dioxide. Although it might be suspected that the maximum in the curve for manganese dioxide was due to an impurity of the manganous oxide, this could not have been true, since Meyer and Rötgers[13] found that manganese dioxide was stable in air at 530°, and the sample used here was heated only to 170°. Furthermore, manganous-manganic oxide is certainly stable at 1100°, and the curve for this substance showed no discontinuity in the temperature range of the experiments.

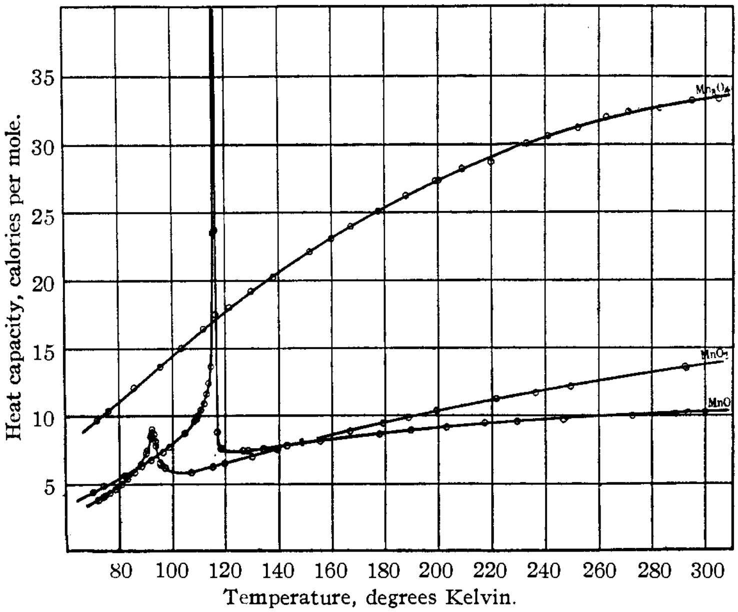

Fig. 1.—The molal heat capacities of MnO, Mn_3O_4 and MnO_2.

Attention should be called to the fact that points on the steep portions of the curves for manganous oxide and manganese dioxide are perfectly reproducible and that the specific heats in the regions of the discontinuities are independent of the history of the substance. Thus, in Table II we note that a continuous series of runs extended from 70.4°K. to 134.5°K., and that the sample was cooled to about 116°K., where two runs were made. The sample was then allowed to come to room temperature, cooled to 92°K. and a continuous series of runs was made from that temperature to room temperature. An examination of Table V shows that the sample was cooled to liquid air temperatures three times—for runs 1, 14 and 30—but that the points obtained near 97°K. fall on the same smooth curve independently of the history of the substance.

Ewald[14] found that ammonium chloride had a higher specific heat between -80 and 0° than between 0 and 50°, but dilatometric measurements in the lower range failed to reveal a volume change. Simon[15] has measured the true specific heat of this salt and found at 242.6°K. a change greatly resembling that of manganous oxide. Parks and Kelley[16] measured the heat effect for a similar change in magnetite at 115°K. Measurements in this Laboratory, soon to be published, show the curve for magnetite to be similar to that of manganous oxide.

In order to calculate the entropy at 298°K., it is necessary to integrate graphically the equation

$$\int \mathrm{d}S = \int C_p \,\mathrm{d}\ln T$$

from 0 to 298°K. Assuming the third law of thermodynamics, $S_0 = 0$, it remained for us to find the area under the plot of C_p against $\ln T$ from 0 to 298°K. Since the lowest of the present measurements is about 70°K., the extrapolation was made with the assumption that at very low temperatures, that is, about 30°K., the equation of Debye gives the specific heat and entropy. In all that follows, the references are to plots of $\log T$ as abscissa and C_p as ordinate.

According to the theory of Born and Kármán,[17] the molal heat capacity at constant volume

$$C_v = \frac{1}{3p}\left[\sum_{1}^{3} D\left(\frac{\beta v_i}{T}\right) + \sum_{j=1}^{3(p-1)} E\left(\frac{\beta v_j}{T}\right)\right] \tag{1}$$

where p is the number of atoms in the molecule, $D(\beta v_i/T)$ and $E(\beta v_j/T)$ represent Debye and Einstein heat capacity functions containing values of frequencies of v_i and v_j, respectively; β is the ratio h/k, where h is Planck's quantum constant and k is Boltzmann's gas constant for 1 molecule. If the frequencies in the three directions are assumed to be the same, the equation reduces to

$$C_v = \frac{1}{p}\left[D\left(\frac{\beta v}{T}\right) + \sum_{j=1}^{p-1} E\left(\frac{\beta v_j}{T}\right)\right] \tag{2}$$

These equations may be expected to hold only at low temperatures; for the substances for which data are shown here, Equation 2 holds only to about 150°K., and it is not expected that Equation 1 will hold at temperatures much higher. No attempts were made to use Equation 1. At very low temperatures the Einstein terms disappear and the heat capacity is represented solely by the Debye terms.

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[14] Ewald, *Ann. Physik,* [4] **44,** 1213 (1914).

[15] Simon, *ibid.,* [4] **68,** 241 (1922).

[16] Parks and Kelley, *J. Phys. Chem.,* **30,** 47 (1926).

[17] Born and Kármán, *Physik. Z.,* **13,** 297 (1912); **14,** 15, 65 (1913); Born, "Dynamik der Kristallgitter," Teubner, Leipzig and Berlin, **1915**.

According to Equation 2 the heat capacity per mole of manganous oxide should be represented by the sum of one Debye and one Einstein function. It was found that the experimental curve (C_p — log T coördinates), extending down to only 70.4°K., could be extrapolated to meet, without an abrupt change of direction, the Debye function of frequency $\beta v = 231$. A curve was then drawn representing the probable course of the curve without discontinuity, and the differences between this curve and the Debye function were plotted. As high as 178°K. these differences could be represented, within the accuracy of the experimental data, by an Einstein function of frequency $\beta v = 502$. Above 178°K. the differences fell below the Einstein curve, instead of above it, as we should expect, since C_p and not C_v was measured. In reality, the values of C_v, if the necessary data for the calculation from C_p were available, would probably not fit the theoretical curves above 150°K.

The entropy at 35.48°K., as given by the Debye function, is 0.514. The area under the curve and its extrapolation to 35.48°K. between this temperature and 298°K. amounts to 14.406. We have, for MnO, $S_{298} = 14.92$ cal./deg.

For manganous–manganic oxide we should have $C_v = D(\beta v_i/T) + 6E(\beta v_j/T)$, where v_j may have the same or different values for the six terms. It was found convenient, however, to represent the data by three Debye and four Einstein functions, using values of $\beta v = 278$ and 611, respectively. The agreement with the data was excellent up to 158°K., and with true values of C_v probably up to 140°K. The Debye entropy below 31.62°K. is 0.704, and the remainder below 298°K. is 35.022. We have for Mn_3O_4, $S_{298} = 35.73$ cal./deg.

For manganese dioxide one Debye function with $\beta v = 268$ and two Einstein functions with $\beta v = 653$ fit the data to 140°K. The Debye entropy below 31.62°K. is 0.257 and the remainder below 298°K. is 13.677. For MnO_2, $S_{298} = 13.93$ cal./deg.

In each extrapolation it was found that even though the Debye curve were shifted along the axis of abscissas to positions so unreasonable that sharp breaks were necessary to join it with the experimental curve, such shifting of the Debye curve did not change the entropy at 298°K. more than 0.1 unit. Simon[15] has shown that it is possible, in fitting theoretical curves to the experimental data on complicated substances, to obtain satisfactory combinations other than those demanded by the Born-Kármán theory, and even to fit the values of C_p rather than those of C_v.

The free energies were calculated from the equation

$$\Delta F = \Delta H - T\Delta S$$

where ΔF is the change in free energy in forming the oxide from its elements, ΔH the heat of formation and ΔS the change in entropy, all at the temperature T.

In order to calculate the entropy of formation, the entropy of oxygen at 298°K. must be known. The calculations of Lewis, Gibson and Latimer[18] give for O_2, $S_{298} = 48.0$ as the weighted mean of 3 values—namely, from Eucken's[19] specific heats and heats of transition of the several forms of oxygen and the third law of thermodynamics, they give Lewis and Gibson's[20] calculation of O_2, $S_{298} = 48.23$; from the data for the reaction $C_G + {}^1/_2O_2 = CO$, they give for O_2, $S_{298} = 45.6$; from the entropy of mercuric oxide and mercury and the entropy change in the formation of mercuric oxide from its elements, they give for O_2, $S_{298} = 49.2$.

Giauque and Johnston,[21] who have recently repeated very accurately the work of Eucken on oxygen, have given 40.8 as a preliminary value of the entropy per mole of oxygen at its boiling point. Millar and Sullivan[22] have calculated, from the data of Scheel and Heuse,[23] the increase in entropy of gaseous oxygen at 1 atm., when heated from the boiling point to 298°K., to be 8.36. The sum, 49.16, agrees almost exactly with the result of Lewis, Gibson and Latimer obtained from the entropy change of the reaction $Hg + {}^1/_2O_2 = HgO$. The value chosen for O_2 is $S_{298} = 49.2$.

The entropy of manganese, $S_{298} = 7.3$, is taken from Lewis and Gibson.[20]

The heats of formation of these oxides have been determined by both Berthelot[24] and LeChatelier[25] with much better agreement than is usual with data of this kind. For manganous oxide Berthelot gives 90,900 cal.; LeChatelier, 90,800. For manganous–manganic oxide both give 328,000, while Ruff and Gersten[26] give 329,000 ± 740. For manganese dioxide Berthelot gives 125,300 and LeChatelier 126,000, while Mixter[27] gives 119,600 cal., but he states that this value is only an approximation, and that LeChatelier, who used pure natural pyrolusite, probably gives a more accurate value for crystalline manganese dioxide. Although the manganese dioxide used in the present investigation was similar to that used by Mixter, Berthelot's value will be used because of errors in Mixter's work which he himself points out.

Table VI exhibits the data used and the resulting values of the free energy of formation of the oxides.

It is hoped that the specific heats necessary to extend these calculations of the free energies of formation to high temperatures will some day be available.

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[18] Lewis, Gibson and Latimer, This Journal, **44**, 1008 (1922).

[19] Eucken, *Ber. deut. physik. Ges.*, **18**, 4 (1916).

[20] Lewis and Gibson, This Journal, **39**, 2554 (1917).

[21] Giauque and Johnston, personal communication.

[22] Millar and Sullivan, *Bur. of Mines Tech. Paper, No. 424*, 1928.

[23] Scheel and Heuse, *Ann. Physik*, [4] **37**, 79 (1912).

[24] Berthelot, "Thermochimie," Vol. II, Gauthier-Villars et Fils, Paris, 1897.

[25] LeChatelier, *Compt. rend.*, **122**, 80 (1896).

[26] Ruff and Gersten, *Ber.*, **46**, 400 (1913).

[27] Mixter, *Am. J. Sci.*, [4] **30**, 193 (1910).

TABLE VI

DATA AND VALUES

Substance	Mn	O_2	MnO	Mn_3O_4	MnO_2
S_{298}	7.3	49.2	14.92	35.73	13.93

Reaction	ΔH	ΔS	ΔF
$Mn + {}^1/_2O_2 = MnO$	−90,900	−17.0	− 85,830
$3Mn + 2O_2 = Mn_3O_4$	−328,000	−84.6	−302,800
$Mn + O_2 = MnO_2$	−125,300	−42.6	−112,600

Summary

The specific heats of manganous and manganous–manganic oxides and of manganese dioxide have been measured from 70 to 300°K.

With the aid of the third law of thermodynamics, the free energies of these substances at 298° K. have been calculated.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY]

THE DIELECTRIC POLARIZATION OF LIQUIDS. III. THE POLARIZATION OF THE ISOMERS OF HEPTANE

BY C. P. SMYTH AND W. N. STOOPS

RECEIVED APRIL 14, 1928 PUBLISHED JULY 6, 1928

Accurate measurements of the dielectric constants of methane, ethane and hexane over a wide range of temperature[1] have made it possible to calculate that the molecules of these substances have no electric moments and calculations made by an approximate method have also indicated the absence of an electric doublet in the molecules of octane and decane.[2] This is in accord with the fact that, according to calculations from molecular structure,[2] it should be possible to replace a hydrogen atom attached to a carbon atom by a methyl group without altering the electric symmetry of the molecule unless the bulk of the methyl group causes distortion of the structure or unless the methyl group itself is distorted due to small shifts of electrons in the field of a doublet already present. Since, with the exception of methane which, as the first member of the series, might be expected to be abnormal, all of the hydrocarbons studied had contained an even number of carbon atoms, it seemed desirable to investigate an odd member of the series, which, of course, would contain an even number of C–C bonds. Measurements made upon pure samples of all of the isomers of heptane very kindly loaned to us by Dr. Graham Edgar of the Ethyl Gasoline Corporation have made it possible to determine the electric symmetry of nine different arrangements of six C–C bonds. An octane, 2,2,4-trimethylpentane, loaned by Dr. Edgar, has also been studied.

[1] (a) Sänger, *Physik. Z.*, **27**, 556 (1926); (b) Smyth and Zahn, THIS JOURNAL, **47**, 2501 (1925); (c) Smyth and Morgan, *ibid.*, **50**, 1547 (1928).

[2] Smyth, THIS JOURNAL, **46**, 2151 (1924).