rated alcohol were 44–47° (lit., 43.5°,[18] 41°[17]) and 74–75° (lit. 72°[19]), respectively.

Fraction 16 had a somewhat higher index than the pure product and the analysis shows this to be due probably to impurities other than hexenol. In any event hardly more than 5% of the total product could have been the isomeric 4-hexenol-2.

Anal. Calcd. for $C_6H_{12}O$: C, 71.94; H, 12.08. Found: C, 70.55; H, 12.17.

Carbonation of the Grignard Reagent Prepared from Methylvinylcarbinyl Chloride.—The Grignard reagent (0.29 mole) prepared from methylvinylcarbinyl chloride (b. p. 62.5–63.0°, $n^{20}D$ 1.1450) was carbonated by pouring the dilute ethereal solution onto a large excess of powdered solid carbon dioxide with stirring. The acidic material was isolated as previously described.[10] Fractionation gave 20.4 g. (70%) of pure 2-methyl-3-butenoic acid, b. p. 101.7–102.0° (50 mm.), $n^{20}D$ 1.4231–1.4233.

Carbonation of Dibutenylmagnesium.—A mixture of dry dioxane (200 g.) and a dilute ethereal solution of butenylmagnesium bromide (0.45 mole) was stirred overnight, then filtered by forcing the pasty mass by nitrogen pressure through a 90-mm. sintered glass filter. The filtrate was carbonated and worked up as in the preceding preparation. Fractionation gave 16.9 g. (37%) of 2-methyl-3-butenoic acid, b. p. 100.9–102.0° (50 mm.), α-phenylethylammonium salt, m. p. 120.5–121.5°.[10]

Summary

1. The addition of formaldehyde, acetaldehyde and acetone to butenylmagnesium bromide results in products of the type $CH_2{=}CHCH(CH_3)$-$C(R)(R')OH$. No detectable amounts of the isomeric unsaturated alcohols were isolated.

2. The carbonation of the butenyl Grignard reagent appears to be independent of the composition of the allylic isomers of the starting halides.

3. The carbonation of dibutenylmagnesium gives a product identical with that obtained from butenylmagnesium bromide.

LOS ANGELES, CALIFORNIA RECEIVED OCTOBER 16, 1944

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[18] Sutter, *Helv. Chim. Acta*, **21**, 1270 (1938).

[19] Cottle and Powell, THIS JOURNAL, **58**, 2270 (1936).

[CONTRIBUTION FROM THE WESTERN REGION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heat Contents at High Temperatures of Magnesium and Calcium Fluorides[1]

BY B. F. NAYLOR[2]

The determination of high-temperature heat content data for metallurgically important substances is part of the program of the Pacific Experiment Station of the Bureau of Mines. This paper presents data recently determined for magnesium and calcium fluorides. Measurements were made for each substance in both the solid and liquid temperature ranges, and the heats of fusion were determined.

Method and Materials

The heat contents were measured by the "drop" method. The apparatus and method were described previously.[3] The calorimeter was calibrated with electrical energy, measured in international joules, and the results were converted to the conventional thermochemical calorie by the relation,[4] 1 cal. = 4.1833 int. joules (NBS). During the measurements, the samples were enclosed in a platinum–rhodium alloy capsule, the heat content of which was known. To prevent loss of the samples at high temperatures, where they tended to "creep" out of the neck, the capsule was sealed with platinum.

Magnesium fluoride was prepared from Baker "C. P. Analyzed" magnesium oxide, containing less than 0.3% Ca and 0.5% SO_4, by treating with hot 48% HF for sixteen hours and then drying at 400°. Analysis for Mg by conversion to sulfate and weighing as $MgSO_4$ gave 38.97% Mg (theoretical 39.02%).

The calcium fluoride was natural fluorite having a very faint purple color. Analysis by treating the ground fluorite successively with HCl and H_2SO_4 and weighing as $CaSO_4$ gave 51.27% Ca (theoretical 51.33%).

Results

Experimental heat contents above 298.16°K. are listed in Table I. The column labeled T, °K. gives the absolute temperature of the sample before it was dropped into the calorimeter, while that marked $H_T - H_{298.16}$ lists the heat liberated per gram molecular weight in cooling from T to 298.16°K. The sample weights were corrected to vacuum, and the molecular weights accord with the 1941 International Atomic Weights.

No attempt was made to correct for the minor impurities present. The lack of premelting and sharp melting point of the calcium fluoride indicated very high purity. Some premelting was observed about 80° below the melting point of the magnesium fluoride, showing it to be somewhat less pure. The experimental heat-content values that appear to involve premelting have been designated "(p)" in Table I.

Heat content values read from smooth curves at 100° intervals, and corresponding graphically computed entropies are given in Table II.

In the region 1,320 to 1,440°K., calcium fluoride shows a decided increase in temperature co-

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[1] Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

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

[3] J. C. Southard, THIS JOURNAL, **63**, 3142 (1941).

[4] E. F. Mueller and F. D. Rossini, *Am. J. Physics*, **12**, 1–7 (1944).

TABLE I

HEAT CONTENTS ABOVE 298.16°K. (CAL./MOLE)

MgF_2 (mol. wt. = 62.32) T, °K.	$H_T - H_{298.16}$	CaF_2 (mol. wt. = 78.08) T, °K.	$H_T - H_{298.16}$
411.3	1,828	370.3	1,237
594.7	4,974	494.1	3,424
712.8	7,130	592.3	5,250
866.0	9,950	746.7	8,220
1032.7	13,110	864.0	10,570
1061.0	13,710	924.0	11,830
1174.0	15,910	1064.1	14,740
1347	19,380	1196.2	17,770
1460	21,760 (p)	1322	21,000
1496	22,730 (p)	1402	23,390
1516	25,010 (p)	1424	24,300
1535	34,100	1447	25,080
1539	37,120	1507	26,850
1582	38,150	1579	28,920
1606	38,780	1606	29,920
1677	40,310	1636	30,560
1702	40,830	1661	31,440
1760	42,180	1684	32,120
		1698	39,630
		1703	39,730
		1710	39,880
		1751	40,900
		1789	41,760

TABLE II

HEAT CONTENTS AND ENTROPIES ABOVE 298.16°K.

	MgF_2		CaF_2	
T, °K.	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg./mole	$H_T - H_{298.16}$, cal./mole	$S_T - S_{298.16}$, cal./deg./mole
400	1,645	4.73	1,755	5.07
500	3,320	8.47	3,540	9.05
600	5,080	11.67	5,400	12.44
700	6,900	14.50	7,320	15.40
800	8,710	16.91	9,280	18.02
900	10,590	19.12	11,300	20.39
1000	12,510	21.14	13,380	22.58
1100	14,450	22.99	15,550	24.65
1200	16,430	24.72	17,850	26.65
1300	18,440	26.32	20,230	28.56
1400	20,460	27.84	22,680	30.37
1424			23,280 (α)	30.80
1424			24,420 (β)	31.60
1500	22,490	29.23	26,660	33.10
1536	23,220 (s)	29.70		
1536	37,120 (l)	38.75		
1600	38,560	39.68	29,620	35.02
1691			32,350 (β)	36.70
1691			39,450 (l)	40.90
1700	40,820	41.04	39,670	41.03
1800	43,080	42.33	42,050	42.38

efficient of heat content, corresponding to a "hump" in the specific heat curve. The heat content curve shows no discernible discontinuity. However, to fit equations to the curve for the purpose of making thermodynamic calculations, the region below 1,424°K. has been designated as "(α)" and the region from there to the melting point as "(β)." Extrapolations of the α and β curves were made, and a value of 1,140 calories calculated as the heat effect at 1,424°K.

From the experimental data, the heats of fusion and melting points of magnesium fluoride and calcium fluoride were found to be 13,900 cal./mole at 1,536°K. and 7,100 cal./mole at 1,691°K., respectively. It is interesting to note that the heat of fusion of the former is almost double that of the latter; similarly, Moore[5] found the heat of fusion much larger for magnesium chloride than for calcium chloride, the values being 10,300 and 6,780 cal./mole, respectively.

The smooth curves and experimental points, together with some data of other investigators, are shown in Fig. 1. The heat effect at 1,424°K. in calcium fluoride and the melting points have been indicated by broken lines.

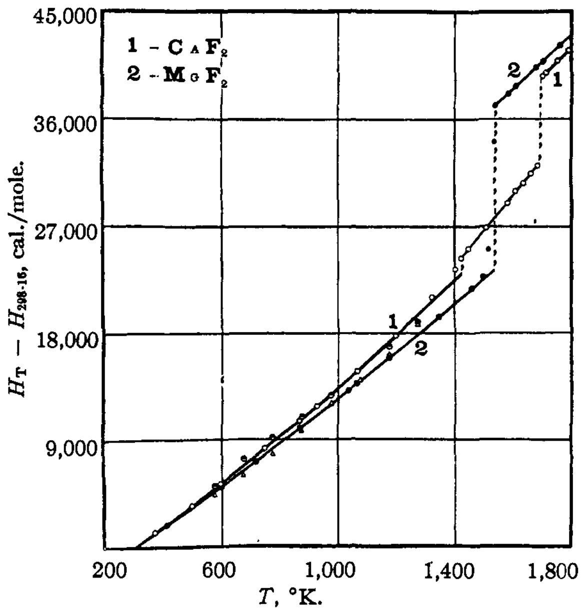

Fig. 1.—Heat contents above 298.16°K.: ● (MgF_2) and ○ (CaF_2), this work; Δ (MgF_2) and ◒ (CaF_2), Krestovnikov and Karetnikov.

Using the data compiled in Table II, heat content equations have been derived and are given below. The equations for magnesium fluoride are based upon the heat contents at 600, 1100 and 1536°K. for the solid and at 1536 and 1700°K. for the liquid. The heat contents at 500, 800 and 1424°K. were used for α-calcium fluoride; at 1424, 1500 and 1650°K. (31,120 calories) for the β-form; and at 1700 and 1800°K. for the liquid. The appropriate temperature range and the mean percentage deviation of the equation from these data are given after each equation.

$MgF_2(s)$: $H_T - H_{298.16} = 16.93T + 0.00126T^2 + (220{,}000/T) - 5898$ (298 – 1536°K.; 0.2%)

$MgF_2(l)$: $H_T - H_{298.16} = 22.57T + 2{,}450$ (1536 – 1800°K.; 0.0%)

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[5] G. E. Moore, THIS JOURNAL, 65, 1700 (1943).

$CaF_2(\alpha)$: $H_T - H_{298.16} = 14.30T + 0.00364T^2 - (46{,}900/T) - 4430$ (298 – 1424°K; 0.3%)

$CaF_2(\beta)$: $H_T - H_{298.16} = 25.81T + 0.00125T^2 - 14{,}869$ (1424–1691°K.; 0.0%)

$CaF_2(l)$: $H_T - H_{298.16} = 23.88T - 930$ (1691–1800°K.; 0.0%)

Differentiating the above heat-content equations gives the specific heat relationships

$MgF_2(s)$: $C_p = 16.93 + 0.00252T - (220{,}000/T^2)$
$MgF_2(l)$: $C_p = 22.57$
$CaF_2(\alpha)$: $C_p = 14.30 + 0.00728T + (46{,}900/T^2)$
$CaF_2(\beta)$: $C_p = 25.81 + 0.00250T$
$CaF_2(l)$: $C_p = 23.88$

Discussion

No reliable values for the specific heats of either fluoride near room temperature appear in the literature. Heat content equations, based upon the first two experimental values obtained at temperatures immediately above 298.16°K. and zero heat content at 298.16°K., were derived for both substances and the specific heats at 298.16°K. obtained by calculation: MgF_2, $C_{p298.16} = 15.8$; and CaF_2, $C_{p298.16} = 17.0$. These derived values may be in error by a few per cent. but they are adequate for many purposes.

The specific heats of both liquid fluorides appear to be constant over the temperature ranges investigated. Measurements of liquid calcium fluoride covered slightly less than 100°, while those of liquid magnesium fluoride extended over about 220°; hence, a small curvature would be imperceptible.

To check the measurements on calcium fluoride in the temperature region 1,320 to 1,440°K., several determinations were made using a sample of reagent grade calcium fluoride. These agreed with the natural fluorite measurements well within the experimental error. Again no discernible discontinuity in the heat content curve was found in this temperature range.

Krestovnikov and Karetnikov[6,7] have made heat content measurements to 1,273°K. on both fluorides. Their results for magnesium fluoride in comparison with the present work are about 7% lower at 573°K., in good agreement at 973° and 1,073°K., and higher by 5% at 1,273°K. Their measurements of calcium fluoride are about 3% higher at 573°K., in fair agreement at 873° and 973°K., and lower by 4% at 1,273°K. They made no measurements in the liquid range of either substance.

Lyashenko[8] has reported measurements of calcium fluoride (not shown in Fig. 1) to 1,590°K. His results are consistently lower than the present work; the average deviation is about 3%.

Summary

High-temperature heat contents above 298.16°K. of magnesium fluoride and calcium fluoride (fluorite) were determined from room temperature to about 1,773°K. From these data heats of fusion and melting points also were obtained. The results have been summarized by algebraic equations and a table giving the heat content and entropy increments above 298.16°K. at 100° intervals.

BERKELEY, CALIF. RECEIVED SEPTEMBER 25, 1944

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[6] A. N. Krestovnikov and G. A. Karetnikov, *Legkie Metal.*, **3**, 29–31 (1934).

[7] A. N. Krestovnikov and G. A. Karetnikov, *ibid.*, **4**, 16–18 (1935).

[8] V. S. Lyashenko, *Metallurg.*, **10**, 85–98 (1935).

NOTES

Complexes of Neutral and Univalent Nickel

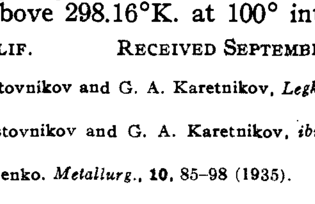
BY CLARA L. DEASY

By treating an anhydrous liquid ammonia solution of potassium cyanonickelate with excess potassium, Eastes and Burgess[1] obtained a compound of the formula $K_4Ni(CN)_4$. With the potassium cyanonickelate in excess, a different compound, $K_2Ni(CN)_3$, was obtained. It was found that the latter compound could also be prepared by treating an aqueous solution of potassium cyanonickelate with potassium amalgam.

No explanation of the state of valence of the nickel in these compounds was offered. On the basis of modern theory, however, electronic formulas for the compounds can be written in the usual way.

The negative radical of the compound $K_4Ni(CN)_4$, $[Ni(CN)_4]^{----}$, is isoelectronic with nickel carbonyl, which also contains neutral nickel. Accordingly an electronic configuration similar to that postulated for nickel carbonyl[2] is suggested. Three resonating structures can be considered:

A



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[1] Eastes and Burgess, THIS JOURNAL, **64**, 1187 (1942).

[2] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 232.