TABLE I

HEAT CAPACITY OF PRIMARY, SECONDARY AND TERTIARY BUTYL ALCOHOL AT 760 MM.

Reference	1-Butanol	2-Butanol	2-Methyl-2-propanol
This paper	34.2 (135°)	34.3 (136°)	36.2 (138°)
This paper	35.5 (162°)	36.6 (158°)	37.8 (160°)
Dobratz[a]	32.6 (135°)	32.6 (135°)	32.6 (135°)
Dobratz[a]	34.1 (160°)	34.1 (160°)	34.1 (160°)
Jatkar[b]	....	....	15.7 (134°)
Bennewitz and Rossner[c]	32.9 (137°)	....	....

[a] Dobratz, *Ind. Eng. Chem.*, **33**, 759 (1941). [b] Jatkar, *J. Indian Inst. Sci.*, **22A**, 39–58 (1939). [c] Bennewitz and Rossner, *Z. physik. Chem.*, **B39**, 126 (1938).

is also lower than that reported by Scott by about 1.5%. Jatkar used the velocity of sound method. He was troubled with considerable absorption and pointed out that some rotational contributions to the heat capacity do not hold at supersonic frequencies. The semi-empirical method of calculation described by Dobratz included contributions to the heat capacity from free rotation about the C–C and C–O bonds. The discrepancy between the calculated and experimental values may be due to a partial association of the alcohols in the vapor state. Determination of the heat capacities at higher temperatures would indicate whether the empirically assigned values of Dobratz are in error.

Summary

A flow calorimeter was designed for measuring the heat capacity of organic vapors when the volume of liquid sample is limited. Not more than 25 ml. is needed and a determination can be made in fifteen minutes. The heat capacities of the three butyl alcohols were also determined at 135 and 160°.

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[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

High-temperature Heat Contents of Manganous Sulfide, Ferrous Sulfide and Pyrite[1]

BY J. P. COUGHLIN

This paper reports the results of high-temperature heat-content (enthalpy) measurements of manganous sulfide, ferrous sulfide and pyrite from 298°K. to the respective temperatures, 1814, 1488 and 980°K. Despite the wide interest in these substances, high-temperature heat content data have been available heretofore only for ferrous sulfide, which was studied in the temperature range 273 to 1473° by Bornemann and Hengstenberg.[2] Anderson[3,4] obtained heat-capacity data for all three substances in the temperature range 55 to 298°K., and Eucken and Schwers[5] studied pyrite between 21 and 84°K.

Materials and Method

Manganous sulfide[6] was prepared from reagent-grade manganous sulfate. The latter was ignited at 950°, leached with water, and reignited. The ignition product was treated for six hours at 750° in a stream of carbon disulfide and carbon dioxide, to produce the sulfide. Absence of free sulfur was proved by subsequent heating in high vacuum at 300°. The final product analyzed 63.15% Mn and 36.88% S, as compared with the theoretical 63.14 and 36.86%, respectively.

Ferrous sulfide was prepared from the pure pyrite, described below, by heating in vacuum at 1000° until sulfur evolution ceased. The product was a single-phase containing 63.04% Fe and 36.90% S, corresponding to the composition $FeS_{1.020}$. Difficulties encountered in an attempt to measure the heat content of a sample on the high iron side ($FeS_{0.970}$, which was found to be two-phase at room temperature and single-phase at higher temperatures) made it inadvisable to try to approach more closely the exact stoichiometric composition. Also it was believed that excess sulfur would help to prolong the life of the container-capsule, making it possible to reach a higher temperature in the heat-content measurements.

The pyrite was a portion of the natural mineral used previously by Anderson[4] in low-temperature heat-capacity measurements. A 20-mesh fraction was screened out, washed twice with hot 1% hydrochloric acid, washed repeatedly with cold water, and finally washed with alcohol–ether and dried in vacuum. Analysis gave 46.51% Fe, as compared with the theoretical 46.55%.

The measurements were made by the "dropping" method with previously described apparatus.[7,8] The samples of manganous sulfide and pyrite were enclosed in platinum–rhodium alloy capsules, which were sealed by platinum welding after evacuating and filling the pore space with helium. The ferrous sulfide was sealed in silica–glass capsules. The heat contents of both types of capsules had been determined in separate experiments. The furnace thermocouple, as usual, was calibrated frequently at the melting point of gold and occasionally at the melting point of palladium.

Results and Discussion

The measured heat content values are listed in Table I and shown graphically in Fig. 1.

Manganous sulfide shows normal behavior from room temperature through the melting point,[9] 1803°K. Two determinations, labeled (a) in Table I, at 1760 and 1802°K., are disturbed

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[1] Article not copyrighted.

[2] Bornemann and Hengstenberg, *Metall u. Erz*, **17**, 339 (1920).

[3] Anderson, THIS JOURNAL, **53**, 476 (1931).

[4] Anderson, *ibid.*, **59**, 486 (1937).

[5] Eucken and Schwers, *Ber.*, **15**, 582 (1913).

[6] Preparations and analyses were conducted by K. R. Bonnickson and R. E. Lorenson, Chemists, Pacific Experiment Station, Bureau of Mines.

[7] Southard, THIS JOURNAL, **63**, 3142 (1941).

[8] Kelley, Naylor and Shomate, *Bur. Mines Tech. Paper* 686 (1946).

[9] Silverman, Morey and Rossini, *Bull. Nat. Research Council*, 107, June 1943.

TABLE I

HEAT CONTENTS ABOVE 298.16°K

T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole
		MnS (mol. wt. 87.00)			
411.1	1355	1078.2	9,835	1329	13,190
513.9	2620	1083.6	9,910	1336	13,250
616.9	3910	1084.4	9,920	1376	13,830
722.6	.5270	1087.7	9,965	1469	15,140
806.2	6350	1105.7	10,220	1562	16,430
822.0	6555	1112.2	10,320	1657	17,840
920.3	7835	1214.3	11,650	1760	19,620(a)
1002.5	8905	1230.0	11,820	1802	22,000(a)
1011.9	8940	1244.7	12,020	1814	26,440
1018.6	9125	1261.3	12,220		
		FeS (mol. wt. 87.92)			
355.8	790	568.8	4,955	1136.4	13,180
366.6	950	599.4	5,550	1146.5	13,360
382.9	1220	610.3	5,745	1218.7	14,410
389.4	1500(b)	623.7	5,925	1227.4	14,570
394.5	1725(b)	634.4	6,090	1314	15,940
403.5	2065(b)	704.2	7,085	1375	16,920
407.9	2175	766.0	7,965	1419	17880(c)
416.5	2305	875.1	9,505	1457	21680(c)
446.9	2845	959.7	10,650	1479	26,260
484.9	3485	1054.9	12,030	1488	26,420
501.8	3780				
		FeS_2 (mol. wt. 119.98)			
404.8	1760	616.8	5,360	869.1	9,980
455.9	2620	695.1	6,725	952.0	11,570
507.5	3515	719.0	7,160	979.9	12,150
553.6	4280	803.6	8,760		

by premelting phenomena. Because of rapid deterioration of the platinum–rhodium container-capsule at the high temperatures, only one measurement was made above the melting point. Although great reliance is not placed in a single measurement, it is worth noting that the indicated heat of fusion at 1803°K. is 6,240 cal./mole.

Crystalline ferrous sulfide undergoes two transitions, at 411 and 598°K., respectively. The heat absorptions calculated from the present measurements are 570 and 120 cal./mole, respectively. Heraldsen[10] has studied these transitions in some detail.

The heat content curve of the lowest-temperature form of ferrous sulfide rises sharply as the 411°-transition is approached. At least a part of this is attributable to excess free sulfur in the lattice.[10] The points labeled (b) in Table I definitely show pretransition effects. The heat content of the intermediate form increases virtually linearly with temperature, the slope being 17.40 cal./deg./mole. Extra sulfur in the lattice does not affect the 598°-transition.[10] The heat content curve for the highest temperature modification follows a normal course. Premelting is exhibited only by the points at 1419 and 1457°K., labeled (c) in Table I. The heat of fusion at the melting point,[9] 1468°K., is 7730 cal./mole.

Bornemann and Hengstenberg[2] reported only even-temperature (°C.) values of the heat content of ferrous sulfide. The information is too incomplete to warrant more than a general comparison with the present work. Omitting their 373°K. value, which appears much too high, the other values for the crystals are lower than the present results by about 1.5% on the average. Their single value in the liquid range (1473°K.)

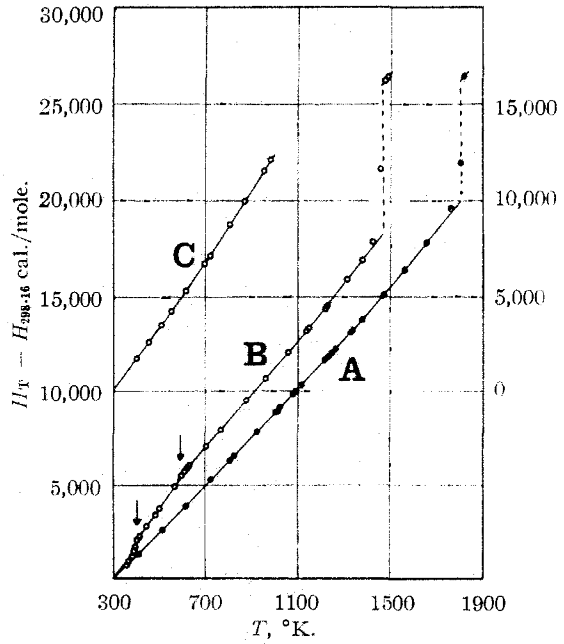

Fig. 1.—Heat contents above 298.16°K.: A, MnS; B, FeS; C, FeS_2 (scale at right).

TABLE II

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

T, °K.	MnS $H_T - H_{298.16}$	MnS $S_T - S_{298.16}$	FeS $H_T - H_{298.16}$	FeS $S_T - S_{298.16}$	FeS_2 $H_T - H_{298.16}$	FeS_2 $S_T - S_{298.16}$
350	....	...	710	2.19	....	...
400	1,220	3.52	1,470	4.21	1,670	4.81
411	....	...	1,640(α)	4.63	....	...
411	....	...	2,210(β)	6.02	....	...
500	2,440	6.24	3,760	9.43	3,350	8.55
598	....	...	5,460(β)	12.53	....	...
598	....	...	5,580(γ)	12.73	....	...
600	3,690	8.52	5,610	12.79	5,060	11.67
700	4,970	10.49	7,020	14.96	6,820	14.38
800	6,260	12.21	8,430	16.84	8,650	16.82
900	7,560	13.74	9,840	18.50	10,550	19.06
1000	8,850	15.10	11,250	19.99	12,520	21.14
1100	10,150	16.34	12,680	21.35		
1200	11,450	17.47	14,150	22.63		
1300	12,770	18.53	15,680	23.86		
1400	14,130	19.54	17,260	25.03		
1468	....	...	18,350(γ)	25.79		
1468	....	...	26,080(l)	31.05		
1500	15,530	20.50	26,620	31.42		
1600	16,970	21.43				
1700	18,450	22.33				
1800	19,970	23.20				
1803	20,020(c)	23.22				
1803	(26,260)(l)	(26.69)				

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(10) Heraldsen, *Z. anorg. Chem.*, **246**, 169, 195 (1941).

appears much too low, indicating that fusion may not have been complete.

The heat content curve for pyrite is regular. At the highest temperature point in Table I, the dissociation pressure is estimated as 1.8 atm. The alloy capsule failed just beyond this point because of increased pressure.

Table II lists smooth values of the heat contents above 298.16°K. at even temperatures and at transition and melting points. The corresponding entropy increments also are listed, having been calculated by the method of Kelley.[11]

The heat content data for the three substances are represented by the relationships below, the temperature range of validity and the average degree of fit being shown in parentheses.

Subst.	$H_T - H_{298.16} =$
MnS(c)	$11.40T + 0.90 \times 10^{-3}T^2 - 3479$ (298–1803°K., 0.5%)
FeS(α)	$5.19T + 13.20 \times 10^{-3}T^2 - 2721$ (298–411°K., 1.0%)
FeS(β)	$17.40T - 4944$ (411–598°K., 0.2%)
FeS(γ)	$12.20T + 1.19 \times 10^{-3}T^2 - 2138$ (598–1468°K., 0.3%)
FeS(l)	$17.00T + 1124$ (1468–1500°K., 0.1%)
FeS_2(c)	$17.88T + 0.66 \times 10^{-3}T^2 + 3.05 \times 10^5T^{-1} - 6413$ (298–1000°K., 1.0%)

Summary

Heat content measurements of manganous sulfide, ferrous sulfide and pyrite were made between 298° and the respective temperatures, 1814, 1488 and 980°K.

Heat content relationships and a table of heat content and entropy increments are reported.

BERKELEY, CALIFORNIA RECEIVED MAY 31, 1950

(11) Kelley, Bur. Mines Bull. 476, 1940, p. 8.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Observations on the Rare Earths. LVIII.[1] Reaction between Neodymium and Ethylenediaminetetraacetate Ions in Aqueous Solution[2]

BY THERALD MOELLER AND J. CALVIN BRANTLEY[3]

Introduction

Comparatively few stable complex species derived from the tripositive rare earth metal ions are known in aqueous solution. In those cases (*e. g.*, with tartrate, citrate, etc.) where the properties of aqueous solutions are indicative of the presence of complex ions, data on stoichiometric compositions are generally lacking. Recent work has emphasized the strong complexing power of ethylenediaminetetracetic acid and has indicated the comparative ease with which systems containing it can be studied.[4-8] It seemed logical to extend studies upon this reagent to systems containing rare earth metal ions, particularly in view of qualitative observations that such systems can be made strongly alkaline without precipitation of the metal ions and are unaffected by normal precipitants for the uncomplexed cations. Reported data on such systems are limited to descriptions of the preparations of compounds of compositions $MH(C_{10}H_{12}N_2O_8)$, M = La, Nd,[6] and $Y_4(C_{10}H_{12}N_2O_8)_2 \cdot 24H_2O$.[7]

Data summarized here are for systems containing neodymium as a typical cerium earth and represent results of spectrophotometric, electrometric and electrophoretic studies.

Experimental

Materials Employed.—Standard aqueous neodymium chloride solutions were prepared[1] from a sample of neodymium oxide which contained no other rare earths. Chemically pure samples of ethylenediaminetetraacetic acid[9] were used as such or as ammonium salt solutions prepared from calculated weights of the acid by titration with aqueous ammonia to *p*H 8.0.

Apparatus.—All absorption spectra were measured with a Beckman model DU quartz spectrophotometer, following the procedure previously outlined.[1] All electrometric titrations were followed with a Beckman model G *p*H meter, the glass electrode of which had been calibrated against standard buffers. Electrophoretic migrations were studied in an H-cell with a sintered glass disc sealed into the cross arm, using platinum electrodes with a current of 0.2 ampere under a potential of 110 volts.

Results and Discussion

Absorption Spectra.—Complete spectra were obtained over the range 2500–10000 Å. for a 1:1 mixture of 0.1312 *M* neodymium chloride and 0.1312 *M* ammonium ethylenediaminetetraacetate solutions and for each of the component solutions. Absorption data were calculated in terms of *k*, the absorption coefficient[1] in the familiar Beer–Lambert relation

$$k = \frac{\log_{10} I_0/I}{cl}$$

c being the concentration in grams of neodymium per liter and *l* being 1.0 cm. Comparison of the

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(1) For the previous communication in this series, see Moeller and Brantley, *Anal. Chem.*, **22**, 433 (1950).

(2) Presented as a portion of the Symposium on the Chemistry of the Less Familiar Elements at the 117th Meeting of the American Chemical Society, Detroit, Michigan, April, 1950.

(3) Linde Air Products Co., Research Laboratory, Tonawanda, New York.

(4) Pfeiffer and Offermann, *Ber.*, **75B**, 1 (1942).

(5) Brintzinger and Hesse, *Z. anorg. allgem. Chem.*, **249**, 113 (1942).

(6) Britzinger, Thiele and Müller, *ibid.*, **251**, 285 (1943).

(7) Brintzinger and Munkelt, *Z. anorg. Chem.*, **256**, 65 (1948).

(8) Schwarzenbach and Biedermann, *Helv. Chim. Acta*, **31**, 459 (1948).

(9) Furnished by the Alrose Chemical Company and the Bersworth Chemical Company, to which concerns the authors express their appreciation.