[CONTRIBUTION FROM THE METALLURGICAL FUNDAMENTALS SECTION, METALLURGICAL DIVISION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

The Specific Heats at Low Temperatures of Anhydrous Chlorides of Calcium, Iron, Magnesium and Manganese[1]

BY K. K. KELLEY[2] AND G. E. MOORE[3]

For the past year or more, the work of the Pacific Experiment Station of the Bureau of Mines has been devoted largely to obtaining thermodynamic data for substances and processes of strategic interest in the present emergency. This work comprises the measurement of low-temperature specific heats, high-temperature heat contents, and heats of solution and formation. The present paper deals with low-temperature specific heats in the temperature range 51 to 298°K. and entropies of the anhydrous chlorides of calcium, iron, magnesium and manganese. Data for these chlorides are of interest in connection with certain hydrometallurgical processes that have been proposed, the metals represented being the principal metallic constituents of an important possible domestic source of manganese.

Materials.—Calcium chloride was prepared by dissolving pure calcite in c. p. hydrochloric acid, followed by evaporation to obtain the hydrated crystals. The hydrated crystals were crushed and slowly heated in vacuum over several days to 130°, which removed most of the water without fusion, although caking occurred. Dehydration was completed in a silica flask in a stream of dry hydrogen chloride, the temperature being raised gradually over several days to 740°. The hydrogen chloride was displaced by dry nitrogen before cooling. The sintered product was removed from the flask and crushed in an agate mortar in a dry-box over phosphorus pentoxide. Analysis showed 35.89% Ca and 63.82% Cl compared with the theoretical figures 36.11 and 63.89%. Magnesium corresponding to 0.59% magnesium chloride was found in the filtrate after the calcium precipitation. A correction for this amount of magnesium chloride was made in the specific-heat results. A 166.35-g. sample was used in the measurements.

Reagent quality ferrous chloride tetrahydrate was heated slowly in vacuum to 200° and then in a stream of dry hydrogen chloride, the temperature being gradually raised to 550°. A small amount of ferric chloride was condensed in the cold neck of the silica flask during the latter process. This was removed, and the material was again heated to 550° in dry hydrogen chloride. No attempt was made to sinter the sample. Analysis gave 44.13% Fe and 55.85% Cl (theoretical figures, 44.06% and 55.94%). Tests for Fe^{+++} using CNS^- were negative. A 147.38-g. sample was used in the specific-heat measurements.

Reagent quality manganous chloride tetrahydrate was heated in vacuum to 200°, the temperature being raised slowly to avoid fusion. Dehydration was completed in a silica flask in a stream of dry hydrogen chloride, the final temperature being 620° where slight sintering occurred. After crushing it was reheated in vacuum to 200°. The manganese content was determined by precipitation as sulfide followed by careful washing and conversion to anhydrous manganous sulfate. Analysis gave 43.42% Mn and 56.30% Cl (theoretical figures 43.65 and 56.35%). Upon the basis of the manganese content, the purity would be 99.5%, which corresponds closely to the analysis of the manufacturer after allowance is made for the water content of the original material. The specific heats were measured on a 188.04-g. sample.

To make magnesium chloride, reagent quality magnesium–ammonium chloride hexahydrate was heated slowly in vacuum to 200° and then in a stream of dry hydrogen chloride to 400° in a Pyrex flask provided with a means of collecting the large amount of ammonium chloride evolved. The material next was transferred to a silica flask and heated for several more days in a stream of dry hydrogen chloride at 500 to 600°. After the final heating at 600°, in which no more ammonium chloride was evolved, the flask was evacuated and cooled. The final product was crushed in a dry-box, as mentioned above. This procedure is essentially the same as that of Richards and Parker,[4] described also by Archibald.[5] Analysis of the product gave 25.74% Mg and 74.25% Cl (theoretical figures, 25.54 and 74.46%). No ammonia was detected on heating in alkali. A water solution of the product gave a slight alkaline reaction. By titration and by conversion to anhydrous magnesium sulfate it was estimated that the material contained the equivalent of 0.2% MgO. Correction was made for this in the specific heat results, which were determined on a 75.03-g. sample.

Specific Heats.—The previously described[6] method and apparatus again were employed. The results, given in Table I, are expressed in defined calories (1 calorie = 4.1833 int. joules). The formula masses used and given in Table I are in accordance with the 1941 International Atomic Weights.

The results also are shown graphically in Fig. 1, in which it is to be noted that the ordinate scale at the right applies only to calcium chloride. The calcium chloride specific heats were corrected for 0.59% magnesium chloride. This correction

---

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

[2] Senior Chemist, Western Region, Bureau of Mines.

[3] Associate Chemist, Western Region, Bureau of Mines.

[4] Richards and Parker, *Proc. Am. Acad. Arts Sci.*, **32**, 53 (1896).

[5] Archibald, "The Preparation of Pure Inorganic Substances," John Wiley and Sons, Inc., New York, N. Y., 1932, pp. 89–91.

[6] Kelley, THIS JOURNAL, **63**, 1137 (1941).

TABLE I

SPECIFIC HEAT OF $CaCl_2$ (MOL. WT. = 110.99)

T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole
52.6	6.362	113.4	12.66	214.6	16.34
55.3	6.706	123.7	13.33	224.7	16.52
58.6	7.150	134.3	13.92	234.9	16.67
62.5	7.658	144.3	14.38	244.8	16.83
66.4	8.197	154.0	14.78	255.0	16.98
70.3	8.685	164.4	15.16	265.7	17.07
80.0	9.783	174.3	15.44	275.8	17.22
84.2	10.22	184.6	15.71	285.8	17.26
93.6	11.12	194.5	15.98	295.1	17.32
103.3	11.93	204.8	16.19		

SPECIFIC HEAT OF $FeCl_2$ (MOL. WT. = 126.76)

T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole
53.2	6.192	115.2	13.39	214.9	17.20
56.7	6.704	125.2	14.07	225.1	17.40
60.8	7.340	135.6	14.68	235.2	17.55
65.2	8.033	145.8	15.17	245.6	17.72
69.3	8.654	155.5	15.59	255.4	17.84
73.6	9.250	165.9	15.96	265.6	17.94
80.6	10.13	175.3	16.27	275.9	18.09
85.5	10.69	185.3	16.56	285.7	18.13
95.4	11.75	195.2	16.82	295.0	18.21
105.1	12.60	205.0	17.00		

SPECIFIC HEAT OF $MgCl_2$ (MOL. WT. = 95.23)

T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole
53.6	4.114	114.2	10.89	215.3	15.58
57.6	4.620	123.9	11.65	225.1	15.81
61.8	5.160	134.9	12.40	235.2	16.02
66.3	5.775	144.6	12.97	245.0	16.21
71.4	6.442	155.3	13.52	255.3	16.40
76.1	7.018	165.1	13.97	266.1	16.56
80.4	7.547	174.6	14.34	276.5	16.74
84.8	8.050	185.1	14.73	286.1	16.84
94.2	9.068	195.0	15.08	295.4	16.98
103.9	9.993	204.8	15.31		

SPECIFIC HEAT OF $MnCl_2$ (MOL. WT. = 125.84)

T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole
53.1	5.522	115.2	12.51	215.5	16.35
56.6	5.987	124.9	13.19	225.8	16.54
60.5	6.557	135.5	13.81	235.9	16.67
64.8	7.199	150.6	14.50	245.8	16.84
68.8	7.784	156.0	14.73	256.1	16.97
73.0	8.349	165.9	15.10	266.0	17.09
80.4	9.249	176.1	15.39	276.0	17.24
85.2	9.795	186.1	15.69	285.7	17.34
95.2	10.85	195.6	15.96	295.0	17.38
104.8	11.70	205.8	16.15		

ranges from 0.06 to 0.16%, depending on the temperature. Likewise, the magnesium chloride specific heats were corrected for the estimated equivalent of 0.2% magnesium oxide. Again, the correction is nearly negligible, 0.06 to 0.18%.

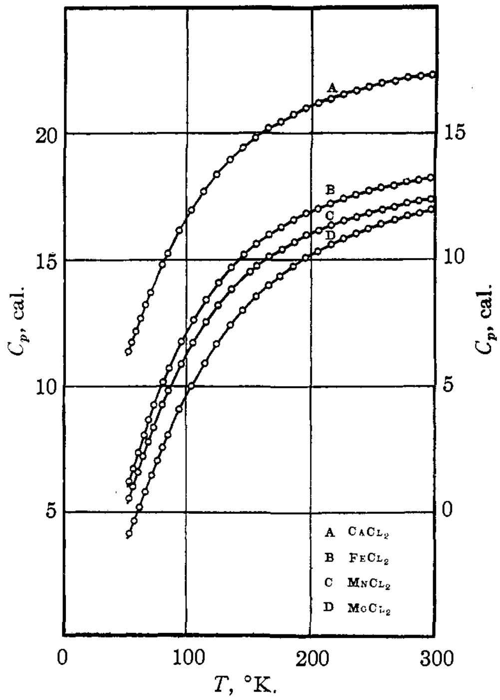


Fig. 1.—Specific heats in calories per gram formula mass. (Scale at right is for $CaCl_2$ only.)

It may be seen from Fig. 1 that in the temperature range studied the four substances exhibit a similar, normal behavior.

Previous low-temperature specific heat measurements of ferrous and manganous chlorides in the range 14° to 130°K. were reported by Trapeznikova and Shubnikow.[7] The work of these authors disagrees with the present results in much the same general fashion as they[8] disagreed with the measurements of Anderson[9] for anhydrous chromic chloride. This is evident from Table II, in which values for comparison are given at a few rounded temperatures.

TABLE II

COMPARISON OF SPECIFIC-HEAT RESULTS

A = Trapeznikova and Shubnikow; B = Anderson; C = This research.

T, °K.	$C_p(CrCl_3)$ $(A - B)$ %	$C_p(MnCl_2)$ $(A - C)$ %	$C_p(FeCl_2)$ $(A - C)$ %
50	13.4	4.0	5.1
75	7.9	3.8	−0.4
100	6.2	4.1	− .9
125	6.7	3.2	− .2

Anderson suggested that the difference might be attributed to lack of purity of the chromic chloride of these investigators, as this substance

---

[7] Trapeznikova and Shubnikow, *Physik. Z. Sowjetunion*, **7**, 66 (1935), and **11**, 55 (1937).

[8] Trapeznikova, Shubnikow and Miljutin, *ibid.*, **9**, 237 (1936).

[9] Anderson, THIS JOURNAL, **59**, 488 (1937).

is difficult to prepare and maintain in pure form. However, now that disagreement is found for two other substances, it appears very probable that the measurements of these workers simply are not accurate. This is immediately evident, at least in part, on plotting their data, which show deviations from a smooth curve amounting to as much as 4%. The results for ferrous chloride in Table II agree better than do the others, but in this instance the deviations of Trapeznikova and Shubnikow's data from a smooth curve are the greatest. It should be mentioned that these investigators found a marked "hump" in the specific heat curve of ferrous chloride near 22.5°K. which undoubtedly is real, as their results for manganous chloride in this region appear mutually normal.

There are no previous pertinent data for calcium and magnesium chlorides.

Entropies.—In calculating the entropies, the lower-temperature portions of the specific heat curves were fitted with a Debye and a pair of Einstein functions as listed below; the temperature range represented is given in parentheses.

$$CaCl_2:\quad D\left(\frac{101}{T}\right) + 2E\left(\frac{294}{T}\right);\quad (51\text{–}130^\circ)$$

$$FeCl_2:\quad D\left(\frac{152}{T}\right) + 2E\left(\frac{266}{T}\right);\quad (51\text{–}100^\circ)$$

$$MgCl_2:\quad D\left(\frac{194}{T}\right) + 2E\left(\frac{349}{T}\right);\quad (51\text{–}140^\circ)$$

$$MnCl_2:\quad D\left(\frac{153}{T}\right) + 2E\left(\frac{295.5}{T}\right);\quad (51\text{–}113^\circ)$$

The appropriate function sums were used to obtain the extrapolated portions of entropy given in Table III for calcium and magnesium chlorides. For ferrous chloride it was estimated from the work of Trapeznikova and Shubnikow that about 2.3 units of entropy over and above that given by the normal specific heat curve are involved in the "hump" at 22.5°K. This amount has been added to the extrapolation given by the function sum to obtain the entropy below 50.12°K. and an extra 0.5-unit error has been allowed for this procedure. It is considered that the "hump" is associated with the uncoupling of the lowest energy level of Fe^{++} in the crystals. The total entropy to be associated with this uncoupling is $R \ln 5 = 3.20$ units of which, it would follow, 0.9 unit has been extracted at 50.12°K. A similar "hump" is to be expected for the uncoupling of the lowest energy level of Mn^{++} in the manganous chloride crystals, but the work of Trapeznikova and Shubnikow shows that it must lie below 14°K. From the calculations of Hull and Hull,[10] it is estimated that the unextracted portion of the uncoupling entropy is at least 3.27 units at 50.12°K. as compared with the total amount $R \ln 6 = 3.56$ units. A similar calculation for Fe^{++} shows that 80% or 2.56 units of the uncoupling entropy should remain at 50.12°K. This agrees, within the limits of error, with the 2.3 units estimated above from Trapeznikova and Shubnikow's rough specific heat measurements. Consequently, 3.3 units has been added to the entropy extrapolated by means of the function sum for manganous chloride to obtain the 6.02 units for 50.12°K., listed in Table III, and an extra 0.5 unit of error has been allowed for this procedure. The extrapolated values for iron and manganese chlorides may be improved by correction when the pertinent data become available. However, the entropies at 298.16°K. given in Table III are more than adequate for use in conjunction with the heat-of-formation data available at present in the calculation of practical free energies of formation or reaction.

TABLE III

ENTROPIES IN CAL./DEG. MOLE

	$CaCl_2$	$FeCl_2$	$MgCl_2$	$MnCl_2$
0-50.12° (extrap.)	4.59	5.19	1.74	6.02
50.12–298.16° (graph.)	22.57	23.46	19.68	21.97
$S_{298.16}$	27.2 ± 0.4	28.7 ± 0.8	21.4 ± 0.2	28.0 ± 0.8

Related Thermal Data.—Free energy of formation values, based upon the entropies in Table III and heat of formation data, are given in Table IV. The heat of formation data are taken from the compilation of Bichowsky and Rossini,[11] ignoring corrections for changing from 291.16° to 298.16°K., all of which are well within the limits of error in these data. The entropies of the elements, used in deriving the entropies of formation, are from the compilation of Kelley.[12]

TABLE IV

FREE ENERGIES OF FORMATION

Substance	$\Delta H_{298.16}$	$\Delta S_{298.16}$	$\Delta F^0_{298.16}$
$CaCl_2$	−190,600	−36.1	−179,800
$FeCl_2$	−81,900	−31.1	−72,600
$MgCl_2$	−153,300	−39.7	−141,500
$MnCl_2$	−112,700	−32.9	−102,900

Summary

Low-temperature specific heat data, in the

---

(10) Hull and Hull, *J. Chem. Phys.*, **9**, 465 (1941).

(11) Bichowsky and Rossini, Thermochemistry of Chemical Substances, Reinhold Publishing Corp., New York, N. Y., 1936.

(12) Kelley, Bureau of Mines Bulletin 434, 1941.

temperature range 51° to 298°K., are reported for $CaCl_2$, $FeCl_2$, $MgCl_2$, and $MnCl_2$ in the anhydrous crystalline state.

The entropy values at 298.16°K. are 27.2 ± 0.4 for $CaCl_2$, 28.7 ± 0.8 for $FeCl_2$, 21.4 ± 0.2 for $MgCl_2$, and 28.0 ± 0.8 for $MnCl_2$.

Free energy of formation values at 298.16°K., computed from entropies and heats of formation, are −179,800 for $CaCl_2$, −72,600 for $FeCl_2$, −141,500 for $MgCl_2$, and −102,900 for $MnCl_2$ (calories per gram formula mass).

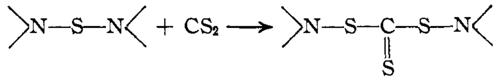
BERKELEY, CALIF. RECEIVED JULY 9, 1942

[CONTRIBUTION FROM THE MONSANTO CHEMICAL COMPANY, NITRO, WEST VIRGINIA]

The Reaction of Carbon Disulfide with Amine Sulfides

BY EDWARD S. BLAKE

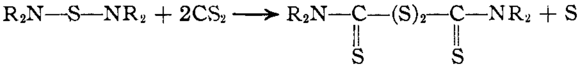
A secondary amine sulfide and carbon disulfide were combined with the expectation of producing trithiocarbonate compounds in accordance with the equation



$$\rangle N{-}S{-}N\langle + CS_2 \longrightarrow \rangle N{-}S{-}\underset{\underset{S}{\|}}{C}{-}S{-}N\langle$$

However, the reaction did not proceed in this manner but rather resulted in the formation of tetra substituted thiuram polysulfides. Furthermore, the course of the reaction is determined by the substituent groups present in the respective amine sulfides.

Aliphatic amine monosulfides, namely, dimethyl and diethyl amine monosulfides, gave the corresponding tetra alkyl thiuram disulfide with the liberation of sulfur; the general reaction is as follows

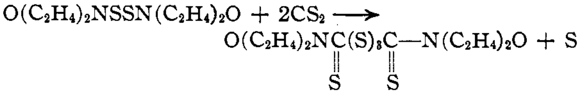


$$R_2N{-}S{-}NR_2 + 2CS_2 \longrightarrow R_2N{-}\underset{\underset{S}{\|}}{C}{-}(S)_2{-}\underset{\underset{S}{\|}}{C}{-}NR_2 + S$$

The yields were 99.1 and 64.8%, respectively, and the purity of the tetra methyl compound was excellent.

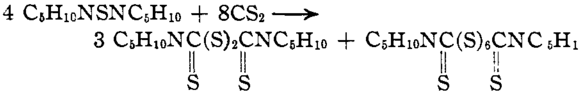
No aliphatic amine disulfides were used because of the difficulty in obtaining these compounds in a high degree of purity since upon purification they are prone to break down into mixtures of amine monosulfide and polysulfides.

The heterocyclic amine sulfides behave differently toward carbon disulfide than do the aliphatic amine monosulfides. Both morpholine mono- and disulfides yield (94 to 96%) the thiuram trisulfide. The monosulfide retains all of its sulfur and the disulfide liberates one atom of sulfur, thus

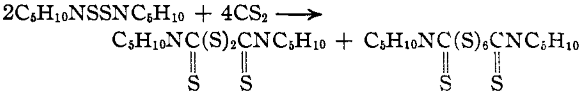


$$O(C_2H_4)_2NSSN(C_2H_4)_2O + 2CS_2 \longrightarrow O(C_2H_4)_2N\underset{\underset{S}{\|}}{C}(S)_3\underset{\underset{S}{\|}}{C}{-}N(C_2H_4)_2O + S$$

Piperidine mono and disulfides reacted strikingly to yield not wholly one product as in the case of the morpholine sulfides but rather to yield a mixture of the thiuram disulfide and the thiuram hexasulfide. The thiuram hexasulfide in both instances is formed in direct ratio to the sulfur present in the amine sulfide reacted.

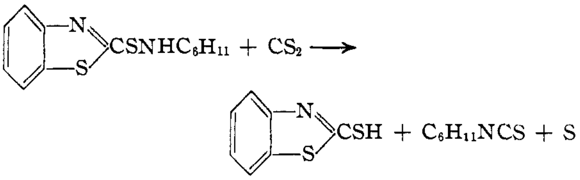


$$4\,C_5H_{10}NSNC_5H_{10} + 8CS_2 \longrightarrow 3\,C_5H_{10}N\underset{\underset{S}{\|}}{C}(S)_2\underset{\underset{S}{\|}}{C}NC_5H_{10} + C_5H_{10}N\underset{\underset{S}{\|}}{C}(S)_6\underset{\underset{S}{\|}}{C}NC_5H_1$$

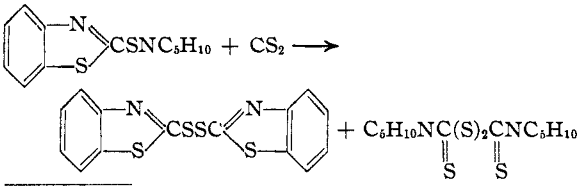


$$2C_5H_{10}NSSNC_5H_{10} + 4CS_2 \longrightarrow C_5H_{10}N\underset{\underset{S}{\|}}{C}(S)_2\underset{\underset{S}{\|}}{C}NC_5H_{10} + C_5H_{10}N\underset{\underset{S}{\|}}{C}(S)_6\underset{\underset{S}{\|}}{C}NC_5H_{10}$$

The action of carbon disulfide on N-substituted 2-benzo-thiazole-sulfenamides, a special type of amine sulfide, proceeds in a manner which again is determined by the substituents present in the amide group. N-Cyclohexyl-2-benzothiazole-sulfenamide, a sulfenamide of a primary amine, reacts[1] to produce 2-mercaptobenzothiazole and cyclohexylisothiocyanate in excellent yields as shown by the equation



2-Benzothiazole-sulfen-piperidide, a sulfenamide of a secondary amine, reacts to yield 2,2′-dithiobisbenzothiazole and cyclopentamethylenethiuram disulfide



---

[1] This reaction was first observed by M. W. Harman, this Laboratory.