three nitrogen atoms, or one azine radical, to form a compound, N_3AgCl, for which the name *azino-silver chloride* is suggested.

Properties of Azino-silver Chloride.—Azino-silver chloride is a blue solid which in the pure state is so deeply colored as to be nearly black. When mixed with varying amounts of silver azide, as happens during its preparation from this substance, it ranges in color through all tints and shades of pure blue. It is stable only at temperatures below −30°, but explodes violently only in the dry state. When moistened with non-aqueous liquids it decomposes rapidly but without explosion when the temperature is raised. It is not particularly sensitive to mechanical shock, but is extremely sensitive to rise of temperature.

When chlorine, ammonia, and sulfur dioxide, respectively, are bubbled through ethereal suspensions of azino-silver chloride at −78°, the compound is at once decomposed, as evidenced by the discharge of the blue color. Qualitative observations indicate that the reactions proceed in accordance with the equations

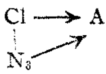
$$2N_3AgCl + Cl_2 \longrightarrow 2ClN_3 + 2AgCl$$
$$6N_3AgCl + 8NH_3 \longrightarrow N_2 + 6NH_4N_3 + 6AgCl$$
$$2N_3AgCl + SO_2 \longrightarrow SO_2(N_3)_2 + 2AgCl$$

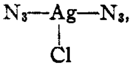
Mechanism and Structure.—It is believed that the first step toward the formation of azino-silver chloride involves the coördination of one molecule of chlorine azide with one of silver azide to form an intermediate product such as

(1) $N_3—Cl \longrightarrow Ag—N_3$

(2) $Cl—N_3 \longrightarrow Ag—N_3$

or

(3) 

The second step may involve a rearrangement that results in the formation of (1) a coördination compound of molecular azine, $(N_3)_2$, with silver chloride, $Cl—Ag \longleftarrow N_3—N_3$, or (2) diazo-silver chloride,  $N_3—\underset{\displaystyle Cl}{\underset{|}{Ag}}—N_3$, in which each of the azine radicals, as well as the chlorine atom, is attached to the silver atom by a normal covalent link, with the result that the silver atom at least temporarily assumes a valence of three.

The third and last step undoubtedly involves the loss of one of the two azine radicals by the intermediate compound, with demonstrable formation of azino-silver chloride, N_3AgCl, in which the silver in all probability is bivalent.

The assumption that silver may assume a valence of two or even three under suitable conditions seems justified (1) by the intermediate position of silver between copper and gold in the periodic system, and (2) by the work of other investigators.[8]

Summary

The interaction of chlorine azide, either in the dry state or in non-aqueous solution, and silver azide has been found to result in the formation of *azino-silver chloride*, N_3AgCl, a deep blue solid compound that is fairly stable at temperatures below −30°, but decomposes into silver chloride and nitrogen at higher temperatures.

Certain of the properties and reactions of this compound have been investigated.

(8) See, for example, (a) Barbieri, *Ber.*, **60**, 2424 (1927); (b) Ruff, *Z. angew. Chem.*, **47**, 480 (1934); (c) Jolibois, *Compt. rend.*, **200**, 1469 (1935), *C. A.*, **29**, 4269 (1935); (d) Braekken, *Kgl. Norske Videnskab. Selskab Forh.*, **7**, 143 (1935), *C. A.*, **29**, 4647 (1935); (e) Noyes and Hoard, THIS JOURNAL, **57**, 1221 (1935).

ITHACA, N. Y. RECEIVED JULY 6, 1943

[CONTRIBUTION FROM THE WESTERN REGION, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR]

Heat Contents at High Temperatures of the Anhydrous Chlorides of Calcium, Iron, Magnesium and Manganese[1]

BY G. E. MOORE[2]

Existing heat capacity and fusion data of inorganic salts at high temperatures are meager and, in most instances, rather unreliable. In particular, extensive data for the liquid state are available in only a few cases. For thermodynamic calculations pertaining to certain metallurgical processes, it would be desirable to have more and better data of this kind. The Pacific Experiment Station of the Bureau of Mines is engaged, in part, in determining high-temperature heat-content data for substances of metallurgical importance; this paper presents such data for four anhydrous chlorides of divalent metals. The solid chlorides were investigated from 25° to their melting points, and the liquid chlorides were studied over temperature intervals of 125° to 660°. The entropies of these compounds have been determined from low-temperature specific-heat measurements.[3]

Materials and Apparatus

The preparation and analysis of the materials have been described.[3] The only impurities to be considered are 0.2% MgO in the $MgCl_2$, for which no correction was made in the present results, and 0.6% $MgCl_2$ in the sample of

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

(2) Chemist, Western Region, Bureau of Mines.

(3) Kelley and Moore, THIS JOURNAL, **65**, 1264 (1943).

TABLE I

HEAT CONTENTS ABOVE 298.16 °K. IN CAL./G. F. W.

$CaCl_2$		$FeCl_2$		$MgCl_2$		$MnCl_2$	
(g. f. w. = 110.99)		(g. f. w. = 126.76)		(g. f. w. = 95.23)		(g. f. w. = 125.84)	
T, °K.	$H^0_T - H^0_{298.16}$	T, °K.	$H^0_T - H^0_{298.16}$	T, °K.	$H^0_T - H^0_{298.16}$	T, °K.	$H^0_T - H^0_{298.16}$
403.7	1,909	670.5	7,210	Series I		668.3	6,968
408.2	2,007	670.8	7,217	653.8	6,590	667.4	6,956
501.0	3,716	909.1	12,070	651.3	6,540	469.7	3,172
504.7	3,788	915.8	12,240	494.1	3,510	467.2	3,114
610.8	5,738	772.0	9,235	872.3	10,820	882.4	11,310
775.6	8,819	487.8	3,646	872.8	10,830	881.9	11,300
777.0	8,849	487.2	3,624	972.5	12,880	907.8(p)	11,880
872.9	10,700	386.6	1,695	979.9	13,030	922.0(p)	13,240
984.8	12,970	386.2	1,660	Series II		765.8	8,916
1038.5(p)	15,800	880.4	11,480	874.5	10,890	568.6	5,026
1018.3(p)	13,870	936.6	12,670	511.6	3,850	952.6	21,830
1070.7	21,600	982.5	24,010	511.1	3,840	1034.6	23,690
1169.5	24,100	978.7	23,880	977.0	12,910	1031.6	23,600
1268.5	26,550	941.0(p)	12,850	786.2	9,110	1148.1	26,200
1449	31,040	1079.7	26,350	786.1	9,120	1201	27,450
1473	31,550	1073.2	26,220	1082.3	25,590		
1553	33,460			1067.1	25,230		
1072.7	21,660			1254	29.380		
992.9	13,120			1276	29,860		
1667	36,120			984.1(p)	13,430		
				1005.6	23,870		
				1427	33,160		
				1428	33,180		

$CaCl_2$, for which correction was applied, amounting to less than 0.1% in the solid range and about 0.2% in the liquid.

The samples were enclosed in sealed platinum–rhodium alloy capsules. After the capsule had been filled with each substance, it was placed in a silica tube having vacuum-tight connections through a rubber stopper for evacuation and leading gas into the neck of the capsule. The tube was pumped out with an oil pump, filled with dry hydrogen chloride, and heated nearly to the melting point of the chloride while a stream of dry hydrogen chloride was kept passing over the material. After about a half-hour of heating at this temperature, the hydrogen chloride was pumped out, and the silica tube was immediately cooled with water. The capsule then was removed, and the neck was pinched shut and welded. This procedure was considered necessary to expel small amounts of water acquired in previous brief exposure of the chlorides to the air, which might cause the development of considerable pressure in the sealed capsule on heating.

Except for the sample of magnesium chloride used in one series of determinations, the samples were fused in the sealed containers before any measurements were made.

The method and apparatus employed have been described previously.[4]

Results

In Table I the measured heat contents above 298.16°K. are given in the order in which they were obtained, in defined calories per gram formula weight (1 calorie = 4.1833 int. joules). The formula weights are in accordance with 1941 International Atomic Weights. The measurements under "Series I" on magnesium chloride were made on a sample that had not been fused. The values designated (p) were considered to involve premelting.

The assignment of accuracy to the data is somewhat arbitrary, but considering contributions from uncertainty in the temperature scale, systematic errors in the calorimetry itself, and those arising from impurities, it is believed that the error is, in general, less than 1%, perhaps increasing to somewhat more than 1% at the lower temperatures (below *ca.* 500°K.). However, the average deviation from a smooth curve in each instance is less than 0.2%.

The measurements on calcium chloride extended to 1670°K., since this substance has a low vapor pressure even at this temperature; for the other three chlorides, however, the vapor pressures become appreciable at much lower temperatures, and the vapors began to escape through minute holes in the container at these temperatures, although the capsules appeared to be gas-tight afterward at room temperature. Consequently, the measurements on magnesium chloride, ferrous chloride and manganous chloride were discontinued when a small leak became evident from a slight loss in weight.

Table II shows heat-content values read at 100°

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

TABLE II

HEAT CONTENTS AND ENTROPIES ABOVE 298.16°K. AT 100° INTERVALS, IN CAL./G. F .W. AND CAL./DEG.-G. F. W.

	$CaCl_2$		$FeCl_2$		$MgCl_2$		$MnCl_2$	
T, °K.	$H^0_T - H^0_{298.16}$	$S^0_T - S^0_{298.16}$	$H^0_T - H^0_{298.16}$	$S^0_T - S^0_{298.16}$	$H^0_T - H^0_{298.16}$	$S^0_T - S^0_{298.16}$	$H^0_T - H^0_{298.16}$	$S^0_T - S^0_{298.16}$
400	1,850	5.32	1,935	5.59	1,800	5.18	1,850	5.32
500	3,700	9.45	3,880	9.92	3,650	9.30	3,730	9.51
600	5,540	12.81	5,800	13.42	5,555	12.77	5,640	12.98
700	7,400	15.68	7,800	16.50	7,480	15.74	7,590	15.98
800	9,290	18.20	9,830	19.21	9,400	18.30	9,600	18.66
900	11,230	20.49	11,880	21.62	11,370	20.62	11,680	21.11
923(s)	. .	. .	.	.	. .	. .	12,160	21.64
923(l)	. .	. .	. .	. .	. .	. .	21,160	31.39
950(s)	. .	. .	12,920	22.75	. .	. .	. .	. .
950(l)	. .	. .	23,200	33.57	. .	. .	. .	. .
987(s)	. .	. .	.	. .	13,160	22.51	. .	. .
987(l)	. .	. .	. .	. .	23,460	32.95		
1000	13,270	22.64	24,410	34.81	23,750	33.24	22,880	33.18
1055(s)	14,420	23.76	. .	. .	. .	. .	. .	. .
1055(l)	21,200	30.18	. .	. .	. .	. .	. .	. .
1100	22,340	31.24	26,860	37.15	25,950	35.34	25,140	35.33
1200	24,870	33.44			28,160	37.26	27,400	37.30
1300	27,320	35.40	L_f = 10,280 ± 50 cal./		30,380	39.04	L_f = 9000 ± 50 cal	
1400	29,800	37.24	g. f. w.		32,590	40.68	g. f. w.	
1500	32,200	38.90	M. p. = 950°K.		34,800	42.20	M. p. = 923°K.	
1600	34,530	40.40			L_f = 10,300 ± 50 cal./			
1700	36,850	41.80			g. f. w.			
	L_f = 6780 ± 80 cal./g. f. w.				M. p. = 987°K.			
	M. p. = 1055°K.							

intervals and at the melting points from the smooth curves through the data, and the corresponding graphically computed entropy increments above 298.16°K. At the bottom of each column, the heat of fusion is given.

The data for calcium chloride show considerable premelting, undoubtedly caused by the 0.6% $MgCl_2$ known to be present; in this instance, allowance was made for additional uncertainty in extrapolating the data for the solid to the melting point to obtain the heat of fusion. The other samples melted quite sharply, there being no evidence of premelting at temperatures more than 15° below the melting points.

The smooth curves obtained from the data are shown in Fig. 1, with some data of other recent investigators, to be discussed below. The following equations were derived from the specific heats at 298.16°K.,[3] the heat contents of the solid and liquid at the melting point of each compound, and other values from Table II. Below about 600°K., the equations for the solids may be in error by 30 to 70 cal.; at higher temperatures and for the liquids, they fit the data within the indicated limits. Equations for C_p may be obtained by differentiation.

(1) $CaCl_2$(s): $H_T - H_{298.16} = 17.18T + 1.52 \times 10^{-3}T^2 + 0.60 \times 10^5T^{-1} - 5459$ (0.7%; 600–1055°K.)
(2) $CaCl_2$(l): $H_T - H_{298.16} = 29.08T - 1.74 \times 10^{-3}T^2 - 7540$ (0.2%; 1055–1700°K.)
(3) or $H_T - H_{298.16} = 24.72T - 4880$ (0.7%; 1055–1700°K.)
(4) $FeCl_2$(s): $H_T - H_{298.16} = 18.94T + 1.04 \times 10^{-3}T^2 + 1.17 \times 10^5T^{-1} - 6134$ (0.1%; 600–950°K.)
(5) $FeCl_2$(l): $H_T - H_{298.16} = 24.42T + 0.0$ (0.1%; 950–1100°K.)
(6) $MgCl_2$(s): $H_T - H_{298.16} = 18.90T + 0.71 \times 10^{-3}T^2 + 2.06 \times 10^5T^{-1} - 6390$ (0.5%; 600–987°K.)
(7) $MgCl_2$(l): $H_T - H_{298.16} = 22.10T + 1650$ (0.1%; 987–1500°K.)
(8) $MnCl_2$(s): $H_T - H_{298.16} = 18.04T + 1.58 \times 10^{-3}T^2 + 1.37 \times 10^5T^{-1} - 5979$ (0.4%; 600–923°K.)
(9) $MnCl_2$(l): $H_T - H_{298.16} = 22.60T + 300$ (0.1%; 923–1200°K.)

Discussion

In the solid range the data are quite regular and need no discussion; the specific heats of liquid manganous chloride and magnesium chloride appear to be constant over the temperature range investigated, and the measurements on liquid ferrous chloride covered only a 100° interval and therefore warrant only the assumption of a straight line. The specific heat of calcium chloride (liquid) is nearly constant but appears to decrease slightly with increasing temperature; that is, the heat-content curve is slightly concave to the temperature axis. The effect is rather small (imperceptible in Fig. 1), and the deviations from the best straight line through the liquid data for $CaCl_2$ exceed the precision by only about 0.5% (*cf.* equations (2) and (3)). At any rate, it can be stated that C_p for calcium chloride (liquid) does not increase with the temperature. It is worth noting, however, that this is apparently the only example of a study of this kind on a fused salt covering such a large temperature interval.

Auzhbikovich[5] (373–1073°K.) and Lyashenko[6] (460–1025°K.) have reported measurements on magnesium chloride; the results of both investigators show what appears to be excessive premelting. Those of the former are higher than the present results by amounts ranging from about 8% at 850°K. to zero at 400°K., and at the lower temperatures their trend would give an impossibly low specific heat at room temperature. On the liquid, Auzhbikovich's results are the higher by 6% at the melting point and 9% at 1073°K.; he gives 10,770 cal./mole for the heat of fusion, in fair agreement with the present result, but his specific heat for the liquid seems to be very high (31.7 cal./mole-deg.). Lyashenko's data are high with respect to the present results by about 1% at 460°K. to 4.5% at 850°K., and his three determinations on the liquid around 1020°K. are high by about 1.8%. He gives 9790 cal./g. f. w. for the heat of fusion.

Krestovnikov and Karetnikov[7] have made measurements on solid $FeCl_2$ (473–913°K.); they are lower than the results reported here by about 15% at 473°K. and lesser amounts with increasing temperatures, becoming the higher by about 4% around 875°K. Their data also exhibit much premelting. They made no measurements on the liquid.

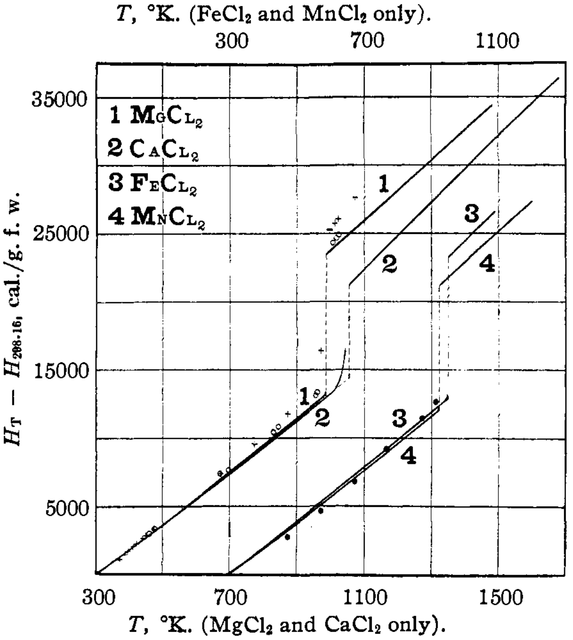

Fig. 1.—Heat contents above 298.16°K. ———, this work; +, Auzhbikovich ($MgCl_2$); O, Lyashenko ($MgCl_2$); ●, Krestovnikov and Karetnikov ($FeCl_2$).

There are no previous pertinent data on calcium chloride or manganous chloride.

Summary

The heat contents of anhydrous calcium chloride, ferrous chloride, magnesium chloride and manganous chloride from room temperature to temperatures between 1080 and 1670°K. have been determined. The heats of fusion of the four chlorides were also obtained from these data.

The data have been summarized by means of algebraic equations and a table giving the heat content and entropy increments above 298.16°K. at 100° intervals.

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[5] Auzhbikovich, *Legkie Metal*, **5**, No. 7, 52 (1936).

[6] Lyashenko, *Metallurg.*, **10**, 85 (1935).

[7] Krestovnikov and Karetnikov, *J. Gen. Chem. U. S. S. R.*, **6**, 955 (1936).