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

The System Ferric Chloride–Sodium Chloride

BY H. F. JOHNSTONE, H. C. WEINGARTNER AND WARREN E. WINSCHE

The existence of a low-melting eutectic containing ferric chloride and sodium chloride has been noted in some recent work[1] on the chlorination of metal oxides by means of sulfur dioxide, air, and sodium chloride. The extremely low vapor pressure of solutions rich in sodium chloride prevents volatilization of the ferric chloride at temperatures up to 600°, nearly three hundred degrees above the boiling point of the pure compound. Because of the low viscosity and heat capacity of the liquid solutions and the long temperature range over which they are stable, the possibility of their use as a heat transfer medium exists. Sander[2] has patented a mixture containing aluminum chloride, sodium chloride, and ferric chloride in the ratio 6:3:1 for this purpose. The use of low-melting chloride mixtures for direct contact chlorination of organic compounds has also been proposed.[3] The solubility of a number of inorganic compounds including the metal oxides in the molten salt mixture indicates that it should also be a suitable reaction medium for inorganic chlorinations.

The low vapor pressures of the system were at first attributed to the existence of a compound. Double salts of ferric chloride have been reported with ammonium chloride,[4] thallium chloride,[5] and lithium chlorides[5a] and with phosphorus pentachloride and phosphorus oxychloride.[6] Herrmann[7] studied the systems cuprous chloride, cadmium chloride, zinc chloride, bismuth chloride and lead chloride with ferric chloride. In each of these the vapor pressure of ferric chloride is strongly depressed by the presence of the other metallic chlorides. While Sainte-Claire Deville[8] showed that a mixture of the anhydrous ferric chloride and sodium chloride fuses below 200°, Neumann[9] was unable to prepare a double salt of this system.

The vapor pressure of pure ferric chloride has been measured by Maier,[10] Stirnemann,[11] Jellinek and Koop,[12] and Sano.[13] No measurements on the vapor pressure of mixtures with other chlorides have been reported, although Naryshkin[14] recently published data on the aluminum chloride–sodium chloride system, showing that the vapor pressure of aluminum chloride is very low when the sodium chloride exceeds 50 mole per cent.

Experimental

The phase diagram for ferric chloride–sodium chloride mixtures was determined by the thermal arrest method and by analysis of the liquid in equilibrium with solid sodium chloride at various temperatures. A small tube furnace, well insulated but having a small heat capacity, was used for heating the salt mixture. The samples were prepared by carefully weighing the pure components to give the desired composition and sealing in Pyrex tubes in an atmosphere of nitrogen. The temperature was measured by means of a calibrated chromel-alumel thermocouple located in a well extending into the center of the salt mixture.

The vapor pressures were determined by the static method, used by Maier. This consisted of maintaining the mixture in a constant volume bulb containing nitrogen at reduced pressure. The pressure was transferred through a capillary mercury U-tube to a manometer system. The partial pressure of the nitrogen in the bulb was calculated from the gas laws after determining the quantity present by means of the observed effect of temperature below the point at which ferric chloride had any measurable vapor pressure. For these measurements the tubes containing the salt mixture were placed in a constant temperature bath consisting of a fused mixture of potassium nitrate, sodium nitrite and sodium nitrate.[15] Thermostatic control was maintained by means of a thermocouple located just below the surface of the ferric chloride–sodium chloride mixture and operating a galvanometer-relay system.

Materials Used.—Ferric chloride was prepared by the action of anhydrous chlorine on pure iron wire. The product was resublimed three times in an atmosphere of chlorine. Precautions were taken to avoid contact with air or moisture at any time during the preparation or the measurements.

In the sublimations the temperature was not allowed to rise above 300° in order to avoid decomposition of the product to ferrous chloride and chlorine.

(1) H. F. Johnstone and R. W. Darbyshire, *Ind. Eng. Chem.*, **34**, (1942).

(2) E. Sander, U. S. Patent 1,971,660 (1934).

(3) E. T. McBee and H. B. Haas, *Ind. Eng. Chem.*, **33**, 137 (1941).

(4) K. Hachmeister, *Z. anorg. Chem.*, **109**, 145 (1919).

(5) G. Scarpa, *Atti Acad. Lincei*, (5) **21**, II, 720 (1912).

(5a) A. Chassevant, *Ann. chim. phys.*, (6) **30**, 21 (1893).

(6) O. Ruff and Einbeck, *Ber.*, **37**, 4518 (1904).

(7) G. Herrmann, *Z. anorg. Chem.*, **71**, 265, 272, 298, 301 (1911).

(8) Sainte-Claire Deville, *Compt. rend.*,, **43**, 971 (1856).

(9) G. Neumann, *Ber.*, **18**, 2891 (1885).

(10) C. G. Maier, U. S. Bur. of Mines Tech. Paper 360 (1925).

(11) E. Stirnemann, *Neue Jahrb. Mineral Geol. Beilage*, **52**, part I, 334 (1925).

(12) K. Jellinek and R. Koop, *Z. physik Chem.*, **145A**, 305 (1929).

(13) K. Sano, *J. Chem. Soc.* (Japan), **59**, 1073 (1939).

(14) I. I. Naryshkin, *J. Phys. Chem.* (U. S. S. R.), **13**, 690 (1939).

(15) W. E. Kirst, W. M. Nagle and J. B. Castner, *Chem. Met. Eng.*, **47**, 472 (1940).

Reagent grade sodium chloride was fused before using and was not subjected to further purification.

The mixtures which were used for the vapor pressure measurements were analyzed subsequently for iron, sodium and chloride by the usual analytical methods.

Data and Results

Phase Diagram.—The temperatures of the arrest points on the cooling curves are shown as open circles in Fig. 1.[16] For samples having compositions less than 45 mole per cent. sodium chloride, there were two well-defined breaks in the cooling curves; but for mixtures richer in sodium chloride, the initial arrest point could not be located either because temperatures high enough to liquefy the sample completely could not be reached in the Pyrex tubes or because the quantity of sodium chloride crystallizing from the melt was too small to cause a noticeable change in the slope of the cooling curve. In all cases, a sharp break occurred in the cooling curves at the eutectic temperature. This was constant over the entire range of compositions studied. The melting points of the mixtures to the left of the eutectic composition are given in Table I. By extrapolation, the composition and temperature of the eutectic is 46.0 mole per cent. sodium chloride and 158°.
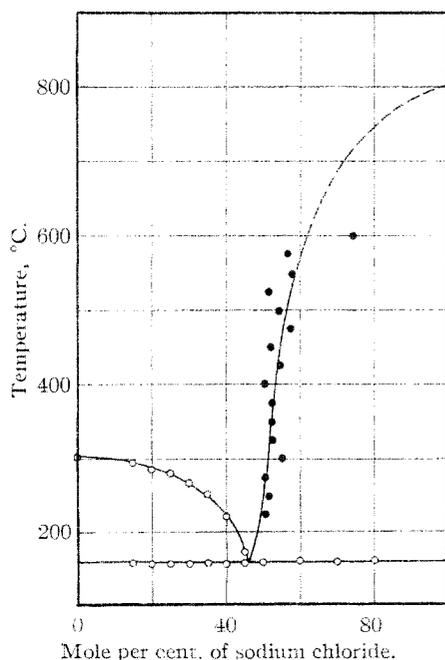

Fig. 1.—Equilibrium diagram of ferric chloride–sodium chloride system.

In order to locate the solid–liquid equilibrium line to the right of the eutectic, an attempt was

(16) Mole percentages throughout are based on the formula FeCl₃.

made to sample and analyze the liquid in contact with the solid at several temperatures. A mixture of ferric chloride and excess sodium chloride was placed in a long open tube in a furnace. Protection against air and moisture was provided by passing a slow stream of nitrogen into the top of the tube. The contents were stirred with the thermocouple tube. Samples of the liquid were withdrawn by means of a hot capillary pipet after the temperature was maintained constant for several hours, the same mixture being used for samples at various temperatures. These were analyzed for sodium, chloride and iron. From the analyses, the composition of the melt was determined and the ratio (3Fe + Na)/Cl was calculated. Positive deviation of this ratio from unity would indicate decomposition of ferric chloride to ferrous chloride. With the exception of three samples taken consecutively at 300°, which were evidently in error, the deviation of this ratio from unity was never greater than 0.02, and both positive and negative values were obtained. Thus the decomposition of these mixtures was negligible even at high temperatures, evidently because of the extremely low vapor pressures. The compositions of the liquid obtained in this way are shown as dots in Fig. 1. Because of the errors inherent in the method of sampling, the points locating the equilibrium line are not as consistent as those obtained by the thermal arrest method. It is evident, however, that the concentration of sodium chloride in the liquid increases only slightly as the temperature is increased nearly 400°. The constancy of the arrest points in the cooling curves is evidence that there can be no break in the equilibrium line up to the melting point of pure sodium chloride.

As further evidence that no stable double salt can exist, the crystals which first formed in the tubes containing the mixtures both below and above the eutectic were separated from the rest of

Table I
Melting Points of Mixtures of Ferric Chloride and Sodium Chloride

Composition, mole % NaCl	Melting point, °C.
0	303
15.0	295
20.0	287
25.0	282
30.0	268
35.0	253
40.0	222
45.0	173

the solution by tilting the tubes. After cooling to room temperature, the tubes were broken open, and these crystals were analyzed without washing. The compositions are shown in Table II. There is no evidence of a compound existing above the eutectic composition.

TABLE II

COMPOSITION OF CRYSTALS FIRST FORMED ON COOLING FUSED MIXTURES OF FERRIC CHLORIDE AND SODIUM CHLORIDE

Composition of mixture, mole % NaCl	Ratio FeCl₃:NaCl in crystals with adhering mother liquor
25.0	4.7
35.0	2.4
45.0	1.2
50.0	0.075
62.5	.061
55.0	.094
60.0	.049
65.0	.035

Vapor Pressures.—The observed vapor pressures of pure ferric chloride and of three mixtures are shown in Table III and in Fig. 2. A mixture containing 49.3 mole per cent. of sodium chloride showed no measurable vapor pressure up to 365°. The data of Maier, Stirnemann and Sano on pure ferric chloride are also shown in Fig. 2. The present data agree more closely with those of Stirnemann than with those of Maier and

TABLE III

VAPOR PRESSURES OF PURE FERRIC CHLORIDE AND OF MIXTURES WITH SODIUM CHLORIDE

Temp., °C.	Pressure, mm.	Temp., °C.	Pressure, mm.
Pure FeCl₃		14.72 Mole % NaCl	
232	9.0	249	33.5
252	30.7	258	67.9
256	43.3	273	137
270	94.9	280	189
282	187.8	294	378
289	267.0	302	396
		309	433
		315	478
		324	544
7.25 Mole % NaCl		44.0 Mole % NaCl	
233	12.1	242	8.6
243	17.0	250	7.0
248	66.5	252	8.5
259	47.1	256	9.8
286	221	263	12.7
297	408	274	15.7
301	523	283	18.6
313	601	290	23.5
320	695	298	28.3
332	845	308	34.9
		322	47.0

Sano. The data of Jellinek and Koop, which consist of four determinations, differ widely from all the other data, and are omitted from the figure.
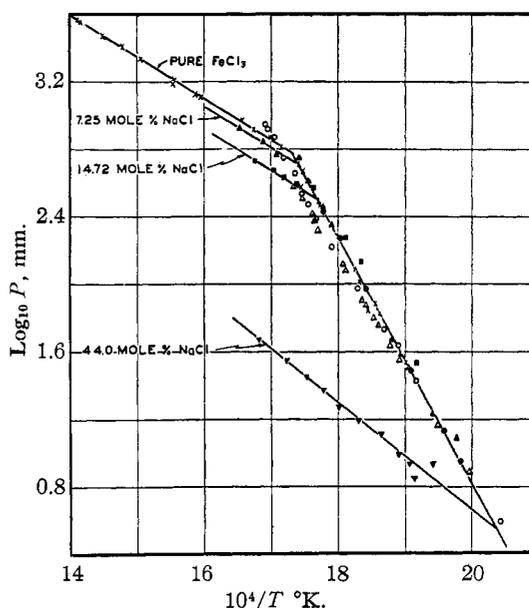

Fig. 2.—Vapor pressures of pure ferric chloride and mixtures of ferric chloride and sodium chloride: pure FeCl₃, ●, authors' data; ×, Stirnemann's data; O, Maier's data; △, Sano's data; ▲, 7.25 mole % NaCl; ■, 14.72 mole % NaCl; ▼, 44.0 mole % NaCl.

Discussion of Results

According to the phase rule, the vapor pressures of solutions in equilibrium with solid ferric chloride should be the same as the sublimation pressure of the pure chloride. On the log p–$1/T$ plot, the vapor pressure lines for the unsaturated solutions at temperatures above the freezing point should be parallel to the line for the pure liquid, provided the heat of solution of molten ferric chloride in the mixture is negligible. The data agree with these predictions for the two dilute solutions but for the concentrated solution there is a definite change in slope of the line.

It is evident from the shape of the equilibrium diagram and from the slope of the lines in Fig. 2 that the vapor pressure of the solutions must decrease rapidly at concentrations above 40 mole per cent. sodium chloride.

For solutions richer than the eutectic and saturated with sodium chloride, the vapor pressure should increase even more slowly as the temperature is raised due to the increasing solubility of sodium chloride. Furthermore, according to Maier, dissociation of the vapor to ferrous chlo-
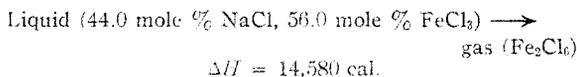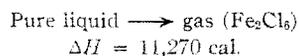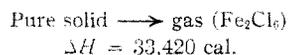
ride and chlorine becomes appreciable above 300°. It is evident, therefore, that ferric chloride cannot be volatilized from a mixture containing excess sodium chloride.

The following heat quantities have been calculated from the vapor pressure data

$$\text{Pure solid} \longrightarrow \text{gas (Fe}_2\text{Cl}_6)$$
$$\Delta H = 33,420 \text{ cal.}$$
$$\text{Pure liquid} \longrightarrow \text{gas (Fe}_2\text{Cl}_6)$$
$$\Delta H = 11,270 \text{ cal.}$$
$$\text{Liquid (44.0 mole \% NaCl, 56.0 mole \% FeCl}_3) \longrightarrow$$
$$\text{gas (Fe}_2\text{Cl}_6)$$
$$\Delta H = 14,580 \text{ cal.}$$

Thus, the heat of solution of solid ferric chloride in a solution having a concentration just below that of the eutectic is 18,840 cal. per gram formula weight of Fe_2Cl_6.

Other Properties.—The molten eutectic mixture conducts electricity readily with the evolution of chlorine at the anode, and reduction to ferrous chloride at the cathode. Corrosion tests were made with various metals in the mixture both exposed to air and in a nitrogen atmosphere. Copper and copper alloys are attacked rapidly. Steel is slightly corroded in moist air. Chromium

alloys and stainless steel are quite resistant to the molten salt.

Summary

1. The phase diagram of the system ferric chloride–sodium chloride was determined. A eutectic, having the composition of 46 mole per cent. sodium chloride, 56 mole per cent. ferric chloride, fuses at 158°.

2. The vapor pressures of pure ferric chloride and of three mixtures with sodium chloride were measured. The observed vapor pressures of solutions saturated with ferric chloride agree with the values reported by Stirnemann for the pure substance.

3. No evidence was found for the existence of a compound between the two chlorides. The extremely low vapor pressure of ferric chloride in the presence of sodium chloride at temperatures above the boiling point of the pure compound is due to the normal effect of the solute in lowering the vapor pressure. This prevents the possibility of volatilizing ferric chloride during chlorination of ores in the presence of excess sodium chloride.

URBANA, ILLINOIS   RECEIVED AUGUST 4, 1941

[CONTRIBUTION No. 186 FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

Activity Coefficients of Strontium Chloride by an Isopiestic Method[1]

BY BENJAMIN A. PHILLIPS AND GEORGE M. WATSON WITH W. A. FELSING

Introduction

The purpose of this investigation was the determination of the activity coefficients of strontium chloride in aqueous solution by the isopiestic method first proposed and used by Bousfield and Bousefield[2] and subsequently improved and made practical by numerous investigators.[3] It was decided to develop this method still further, contemplating certain changes in the ap-

paratus which would increase the accuracy of the determinations.

The reference electrolyte chosen for use in this study was barium chloride, the activity coefficients of which have been determined with highly satisfactory agreement by the different methods of Tippetts and Newton,[4] by Newton and Tippetts,[5] and by Robinson.[6] Harned and Åkerlöf[7] have recalculated the data of Lucasse,[8] and Pearce and Gelbach[9] have presented a limited number of values.

Experimental determinations of the activity coefficients of strontium chloride are not numerous. Lucasse,[8] Hepburn[10] and Harned and

(1) Constructed from a portion of a thesis presented to the Graduate Faculty of the University of Texas by Benjamin A. Phillips in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1939. Original manuscript received October 7, 1940.

(2) Bousfield and Bousefield, *Proc. Roy. Soc.* (London), **A103**, 429 (1923).

(3) (a) Sinclair, *J. Phys. Chem.*, **37**, 495 (1933); (b) Robinson and Sinclair, THIS JOURNAL, **56**, 1830 (1934); (c) Robinson, *ibid.*, **57**, 1161, 1165 (1935); (d) Robinson and Jones, *ibid.*, **58**, 958 (1936); (e) Robinson, *ibid.*, **59**, 84 (1937); (f) Robinson, *Trans. Faraday Soc.*, **34**, 1142 (1938); (g) Owen and Cook, THIS JOURNAL, **59**, 2273 (1937); (h) Mason and Ernst, *ibid.*, **58**, 2032 (1936); and (i) Mason, *ibid.*, **60**, 1638 (1938).

(4) Tippetts and Newton, *ibid.*, **56**, 1675 (1934).

(5) Newton and Tippetts, *ibid.*, **58**, 280 (1936).

(6) Robinson, *ibid.*, **59**, 84 (1937).

(7) Harned and Åkerlöf, *Physik. Z.*, **27**, 424 (1936).

(8) Lucasse, THIS JOURNAL, **47**, 752 (1925).

(9) Pearce and Gelbach, *J. Phys. Chem.*, **29**, 1023 (1935).

(10) Hepburn, *J. Chem. Soc.*, 1204 (1932).