means of a 1P22 photomultiplier tube at the exit slit of a constant-deviation spectrometer. The emission spectrum of Fig. 6 shows two peaks, the first at 4925 Å. and the second at 5375 Å. This emission spectrum is similar to that of Standard VII, but is shifted by about 100 Å. in the direction of longer wave lengths.

On comparison of the emission and absorption spectra, it can be seen that the peak of the emission spectrum at 4925 Å. corresponds to a region of strong absorption in the visible absorption spectrum. This may be at least a partial explanation for the decrease in brightness when the activator concentration is increased beyond the optimum value. This self-absorption, while not necessarily the only factor, seems to play an important part in the diminution of brightness after reaching the peak of the brightness–concentration curves.

Summary

1. Pure, oxide-free magnesium sulfide has been prepared and used to prepare infrared-sensitive phosphors by activation with rare-earth pairs, both with and without fluxes.

2. On the basis of indications as to the low solubility of magnesium sulfide in the flux, it is suggested that a major function of the flux is to act as a recrystallizing agent for the base material, incorporating the activators during the process.

3. Measurement of emission and absorption spectra indicate that self-absorption, due to the overlap of the absorption and emission bands, accounts in part for the maxima observed in brightness–activator concentration curves.

BROOKLYN 2, N. Y. RECEIVED NOVEMBER 29, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AT THE UNIVERSITY OF WASHINGTON]

An Equilibrium Study of the Thermal Dissociation of Ferric Bromide

BY N. W. GREGORY AND BETTY A. THACKREY

The anhydrous ferric halides may be thermally decomposed into free halogen and the corresponding ferrous compounds. The ease of decomposition increases markedly in the order expected from a consideration of the size and electron affinity of the halogen concerned. Ferric fluoride does not decompose appreciably until the temperature is above 1000°[1]; ferric chloride begins to decompose materially at its normal boiling point (319°)[2]; ferric bromide cannot be sublimed unless a pressure of bromine in excess of one atmosphere is maintained in the system; and solid ferric iodide has not been prepared as yet.

In connection with a general program of study of the thermodynamic properties and structures of iron halides, we have investigated the equilibrium $FeBr_3(s) = FeBr_2(s) + 1/2Br_2(g)$ in the temperature interval 65–140°.

Experimental Part

(a) **Reaction of Iron and Bromine.**—Crystalline ferric bromide was prepared by the bromination of iron powder. The reaction vessel consisted of a pyrex tube bent in the shape of an inverted "V." Iron was introduced into one arm of the tube, and the other connected to a vacuum line and a supply of anhydrous bromine. After thorough outgassing, bromine was sublimed into the evacuated reaction vessel and condensed there by means of a liquid-air-bath. The tube was then sealed off and the bromine transferred to the arm opposite the iron. The temperature of the iron was increased to 175–200° and that of the bromine to 120° by means of separate furnaces which came into contact at the apex of the tube. At 120° the vapor pressure of bromine is approximately five atmospheres.[3] Under these conditions ferric bromide can be sublimed away from the iron and will collect in the form of beautiful black shiny plates just beyond the 200° furnace. A small amount of yellow crystalline ferrous bromide will be observed at the end of the furnace if the bromine pressure is not maintained sufficiently high, or if the furnace heating the iron is kept at higher temperatures. The rate of sublimation can be materially increased under the latter condition.

Iron will react quite readily with bromine at lower temperatures. A mixture of liquid bromine and iron powder react very noticeably at room temperature, causing vigorous boiling of the bromine. Ferric bromide forms under these conditions, yielding a black crystalline product which is very hygroscopic. However, it was found almost impossible to get complete conversion of the iron particles into ferric bromide unless the latter is sublimed away from the reaction zone. If this is not done, the ferric bromide forms a protective coating about the iron particles which prevents further attack by bromine. In one instance a mixture of iron and bromine was allowed to stand for several weeks at room temperature. At the end of this period the iron appeared to have reacted completely; however, upon dissolving the sample it was found that nearly one-half of the iron powder remained trapped inside the crystallne product.

The samples of ferric bromide used for the equilibrium study were prepared independently and analyzed by standard methods. They were found to possess Fe/Br ratios between 1:2.97 and 1:3. Measurements were not made beyond 122° for sample 1 as an insufficient quantity of material was introduced into the apparatus to establish an equilibrium pressure of bromine beyond this temperature. A relatively large excess of ferric bromide was used in the second series of measurements.

(b) **Equilibrium Measurements.**—The solid ferric bromide was transferred in a dry box into a glass membrane manometer.[4] The manometer consisted of a very thin walled pyrex bulb, flattened on one side, with a slender glass rod (10 cm. long) sealed on to the flat surface to act as a pointer to detect motion of the membrane. The thin walled bulb was inserted by means of a ring seal into a pyrex tube and connected to the vacuum line and manometer in the usual manner. The sensitivity of the gage was such that pressure measurements could be made with an uncertainty of not more than ±1 mm. The position of the pointer at the null point was found to be independent of temperature and pressure over the range of interest.

After introduction of the sample, the apparatus was

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[1] K. Jellinek and A. Rudat, *Z. anorg. allgem. Chem.*, **175**, 281 (1928).

[2] C. G. Maier, U. S. Bureau of Mines Bulletin, T. P. 360 (1925).

[3] "Int. Crit. Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1938, p. 201.

[4] F. Daniels, THIS JOURNAL, **50**, 1115 (1928).

evacuated to a pressure $< 10^{-5}$ mm. and sealed off after allowing an appreciable period for outgassing. The apparatus was surrounded by an electric furnace designed to maintain uniform and constant temperature.[5] Temperatures were measured by means of chromel–alumel thermocouples which in turn were checked against thermometers calibrated by the National Bureau of Standards.

The system was maintained at constant temperature with the aid of a thermal regulator for a period sufficient to attain equilibrium. For the lowest temperatures, several days were required for the decomposition reaction to establish a constant pressure, whereas several weeks were necessary for the recombination reaction to reach equilibrium. At higher temperatures, equilibrium was established in a few hours. Because of the slow recombination reaction at lower temperatures, the equilibrium was not approached from the high pressure side below 95°. However, the data obtained at low pressures from the initial decomposition reaction agree well with the curve established from both sides at higher temperatures.

Results and Discussion

The data in Table I were obtained from the two samples described above, prepared independently, and tabulated in the order in which measurements were made.

TABLE I

EQUILIBRIUM PRESSURE OF BROMINE OVER FERRIC BROMIDE

Sample 1				Sample 2			
t, °C.	*P*, mm.	*t*, °C.	*P*, mm.	*t*, °C.	*P*, mm.	*t*, °C.	*P*, mm.
75	21	113	200	78	26	125	397
90	55	107	146	88	49	133	579
100	98	98.5	93	108	158	138	748
112	183	94.5	78	123.5	357	134.5	645
119	280	118	255	128	454	67	13[a]
				133.5	656	75.7	22

[a] Bromine pumped out of apparatus between these points.

Several factors must be considered in the interpretation of these data. One concerns the nature of the gas phase in the equilibrium vessel. The vapor pressure of ferric bromide is believed to be negligible for the following reasons. It has not been found possible to get appreciable sublimation of ferric bromide in a reasonable length of time at the highest temperature used in the equilibrium study. The vapor pressure is sufficient at 150° to transfer approximately one-half gram of $FeBr_3$ three inches down a tube of 0.5 inch diameter in a period of twenty-four hours, with the bromine pressure in the system held at 1000 mm. On the basis of this observation and the lack of any apparent curvature in Fig. 1 at the high temperature end, it has been assumed that the entire pressure generated in the apparatus may be attributed to bromine without introducing an appreciable error at the temperatures used in this investigation. It may also be noted, by way of comparison, that the vapor pressure of ferric chloride at 140° is approximately 10^{-4} mm.[2]

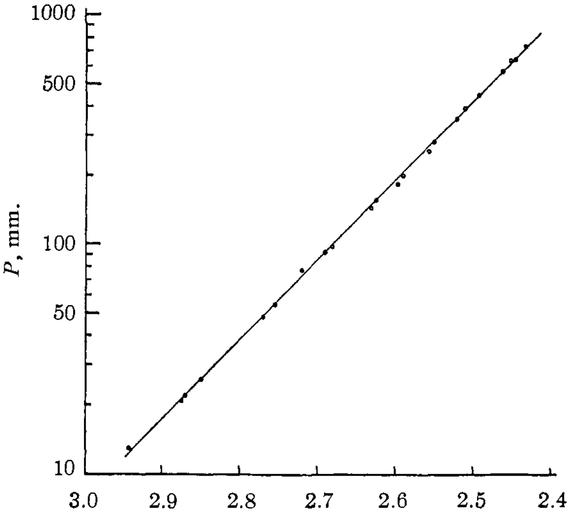

Fig. 1.—Equilibrium pressure of bromine over solid ferric bromide.

The nature of the product formed as a result of the thermal decomposition of ferric bromide has been considered carefully. It has been established independently that heating ferric bromide in vacuum leads to the release of bromine with subsequent sublimation of ferrous bromide at temperatures of the order of 400°. In the measurements made with sample 1, evolution of bromine was complete at 122°. Further heating of this sample to 450° in the equilibrium apparatus did not bring about an abnormal increase of bromine pressure in the system. Hence the sample is considered as having gone completely from ferric bromide to ferrous bromide in the equilibrium vessel as the temperature was increased to 122°. Some decomposition presumably occurred during the outgassing before the apparatus was sealed off; however, analysis of the sample after measurements were completed demonstrated that this loss was relatively small.

Since the data obtained from sample 1 agree well with those of sample 2, where a large excess of ferric bromide was introduced initially, it is concluded that intermediates such as Fe_3Br_8[6] are not involved and that a solid solution is not formed in the system under the conditions employed. On the basis of these observations the data have been interpreted as characterizing the equilibrium $FeBr_3(s) = FeBr_2(s) + 1/2\, Br_2(g)$.

We are unable to offer evidence at this time as to whether the ferrous bromide formed in the decomposition is macrocrystalline or colloidal. Giauque[7] has recently observed that particle size can have a significant effect on the thermodynamic properties of such systems. Whereas the vapor pressure of ferrous bromide is too low at the temperatures concerned to expect crystal formation to occur at a reasonable rate, it is possible that crystal growth is facilitated by the

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[5] E. L. Wiseman and N. W. Gregory, THIS JOURNAL, **71**, 2344 (1949).

[6] F. Oberhauser and J. Schormuller, *Ber.*, **62B**, 1485 (1929).

[7] W. F. Giauque, THIS JOURNAL, **71**, 3192 (1949).

simultaneous deposition and decomposition of ferric bromide vapor. This phase of the equilibrium study is being investigated further.

The straight line drawn in Fig. 1 represents the equation of the form log P(mm.) = $-A/T + B$, where the constants were determined from the data by the method of least squares (A = 3478.6; B = 11.327). From this equation ΔH^0 for the reaction $2FeBr_3(s) = 2FeBr_2(s) + Br_2(g)$ is found to be 15.9 kcal. at an average temperature of 102°. The average deviation of log P (experimental) from log P calculated from the least squares solution is 0.0102. This corresponds to a mean deviation of P of 2%. The estimated uncertainty in ΔH^0 is ±0.4 kcal.

The data obtained are not sufficiently precise to determine ΔC_p for the reaction. Since this factor is expected to be small on the basis of comparison with similar reactions, the heat of formation of ferric bromide has been calculated at 25° assuming that $\Delta C_p = 0$, and using a value of −60 kcal./mole for the heat of formation of ferrous bromide.[8,9] Table II contains a summary of the thermodynamic constants at 25° obtained by extrapolation of these data (liquid bromine taken as standard state; S^0 (Br_2 liq.) = 36.7 e. u.).[10] ΔS^0 is somewhat less than one would expect from Latimer's rule; however, this does not appear to be uncommon for compounds of this type.

TABLE II

THERMODYNAMIC PROPERTIES OF THE IRON BROMIDES

	ΔH^0_{298}, kcal.	ΔF^0_{298}, kcal.	ΔS^0_{298} cal./-mole/deg.
$FeBr_3(s)-FeBr_2(s)$	− 4	−1.8	9.8
$FeBr_3(s)$	−64		

From the extrapolated value of ΔF^0, it is observed that ferric bromide is thermodynamically stable at room temperature if the bromine pressure in the system is greater than 0.5 mm. The equilibrium pressure of bromine reaches one atmosphere at 139°. These factors must be considered in the preparation and handling of anhydrous ferric bromide.

Summary

The thermal dissociation of ferric bromide has been studied in the temperature interval 65–140°. The data have been interpreted as characterizing the equilibrium $FeBr_3(s) = FeBr_2(s) + 1/2Br_2(g)$. The results may be summarized as follows: log $P^{1/2}$mm.(Br_2) = $-(1739.3/T) + 5.663$. At 25° (extrapolated), ΔH^0 = 8.0 kcal.; ΔF^0 = 2.2 kcal.; ΔS^0 = 19.5 cal./mole/deg.

SEATTLE 5, WASHINGTON RECEIVED DECEMBER 28, 1949

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[8] F. R. Bichowsky and F. D. Rossini, "Thermochemistry of Chemical Substances," Reinhold Publ. Co., New York, N. Y., 1936, p. 90.

[9] H. Hieber and A. Woerner, *Z. Elektrochem.*, **40**, 287 (1934).

[10] K. K. Kelley, U. S. Bureau of Mines, Bull. 434 (1940).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Partial Hydrolysis of Silicon Tetrachloride

BY WALTER C. SCHUMB AND ARTHUR J. STEVENS

In a preliminary communication[1] it was shown that by the partial hydrolysis of silicon tetrachloride, dissolved in anhydrous diethyl ether, by means of moist ether, the first two members of the homologous series of oxychlorides, $Si_nO_{n-1}Cl_{2n+2}$, could be prepared, namely, Si_2OCl_6 and and $Si_3O_2Cl_8$. The existence of such homologous series of silicon oxychlorides and of oxybromides, prepared by other methods, had been established definitely in earlier papers from this Laboratory.[2,3] These results showed sufficient promise to warrant a more extensive study of the hydrolysis reaction carried out under various conditions. In the preliminary notice it had been reported that attempts to effect partial hydrolysis in the vapor phase were unsuccessful. It had also been observed that while partial hydrolysis in ether and in *p*-dioxane was possible, the use of other liquids as solvents, such as benzene, toluene, chloroform, pentene-1, and petroleum ether, led only to the formation of silica. The significance of these facts led us to undertake a systematic study of the reaction in an attempt to determine the role of the ether and the optimum conditions for carrying out the reaction leading to the oxychlorides.

The effect upon the course of the reaction of three molar ratios was studied—the silicon tetrachloride–water ratio, the ether–water ratio, and the ether–silicon tetrachloride ratio. A knowledge of these three ratios prevailing in the separate experiments, considered together with the proportions of the products obtained, should throw light upon the part played by the ether and other theoretical aspects of the hydrolytic process.

Because of the ease of separation and measurement of the quantities of Si_2OCl_6 formed, the quantitative interpretation of the experimental results was based upon the yields obtained from this first member of the homologous series; the higher members being reported as a mixture of known silicon, oxygen and chlorine content. The average chain lengths of the mixtures of oxychlorides of higher molecular weight than Si_2OCl_6 were also calculated from the elementary analysis of the mixture, as discussed below.

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[1] Schumb and Stevens, THIS JOURNAL, **69**, 726 (1947).

[2] Schumb and Klein, *ibid.*, **59**, 261 (1937).

[3] Schumb and Holloway, *ibid.*, **63**, 2753 (1941).