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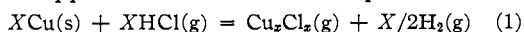
## The Thermodynamics of Gaseous Cuprous Chloride, Monomer and Trimer<sup>1</sup>

BY LEO BREWER AND NORMAN L. LOFGREN

The present interest in cuprous halide gaseous molecules, generally considered to be dimeric, is the result of the following observations on existing experimental data. In reporting the vapor pressure of liquid cuprous halides, Kelley<sup>1a</sup> noticed the abnormally low entropy of vaporization, unexplained by a dissociation into a monomeric molecule. In addition, from our analysis of vapor density measurements by Wartenberg and Bosse,<sup>2</sup> Meyer and Meyer,<sup>3</sup> and Biltz and Meyer<sup>4</sup> who obtained values for the molecular weights of cuprous chloride vapors at elevated temperatures, something unusual was suspected. The results of the three molecular weight determinations give values 213–216 at 1450°, 204 at considerably above 1000° and 187–192 at about 1650°, respectively, compared with a theoretical value of 198 for the dimer. What was presumed to be a possible irregularity was the unusual stability of the dimer, which species previously has been assumed because of the grouping of these molecular weights about 198.

Maxwell and Mosley<sup>5</sup> were unable to arrive at any conclusions in an attempt to interpret electron diffraction measurements assuming a monomer or dimer. Their results, which indicate at least two interatomic distances, show the polymer molecule to be non-linear.

Consequently, this paper is concerned with the investigation of the equilibria in the cuprous halide vapors as well as the determination of the thermodynamic properties of these species in order to ascertain the causes for the fore-mentioned anomalies. Briefly, the experimental procedure consisted of the investigation of the following equilibrium brought about by passing a mixture of hydrogen and hydrogen chloride over copper metal at elevated temperatures.



By means of the relation between the cuprous chloride volatility and the ratio ( $P_{HCl}/P_{H_2}^{1/2}$ ) the polymer number  $X$  was satisfactorily evaluated giving results which were confirmed quite conclusively by remeasurement of the molecular weight of cuprous halide vapor at temperatures lower than in the previously mentioned work. From the equilibrium data collected the evaluation of the free energy, heat and entropy of reaction (1) was possible.

(1) From the Ph.D. Thesis of Norman L. Lofgren: presented at Sept., 1948, Portland, Ore., meeting of American Chemical Society.

(1a) K. K. Kelley, Bureau of Mines Bulletin No. 383 (1935).

(2) H. V. Wartenberg and O. Bosse, *Z. Elektrochem.*, **28**, 384 (1922).

(3) V. Meyer and C. Meyer, *Ber.*, **12**, 1112 (1879).

(4) H. Biltz and V. Meyer, *ibid.*, **22**, 725 (1889).

(5) L. R. Maxwell and V. M. Mosley, *Phys. Rev.*, **55**, 238 (1939).

### Experimental

**Materials.**—Anhydrous hydrogen chloride as received from the Matheson Company was employed in the synthesis of the hydrogen–hydrogen chloride mixtures.

Electrolytic copper metal with a silver content less than 0.1% was used.

Anhydrous cuprous chloride was prepared from copper metal and anhydrous hydrogen chloride in a quartz tube at 800 to 1000° from which the gaseous cuprous chloride would volatilize and re-condense in cooler portions of the tube in the presence of the resulting hydrogen–hydrogen chloride mixture. This fused product was very stable in dry air and quite stable in atmospheric air for periods of several days.

**Molecular Weight Apparatus.**—(a) The gas saturation apparatus consisted of a quartz tube 15 mm. outside diameter and 5 cm. long joined at each end by quartz capillary tubing to minimize diffusion. The central section containing the pure cuprous chloride solid was placed in an electrically controlled furnace. Argon was used as a carrier gas, and the volume flow was measured by displacement of water in an inverted 500-cc. buret. On the exit capillary a tube of larger bore was attached ten cm. from the vaporization chamber to allow space for the condensed cuprous chloride. The gas velocity in the capillary was calculated to be approximately ten cm. per second and the time of exposure of the argon to the liquid halide was nearly one-half a minute. Analysis of the material was procured by breaking the exit tubing at the ten cm. position and rewelding after the sample had been removed. Temperature was measured by a chromel–alumel thermocouple calibrated at the m. p. of copper metal in graphite.

(b) The second apparatus consisted of a fifty cc. quartz cell approximately ten cm. long with optical quartz windows at each end. The weighted sample of cuprous chloride was placed in the previously dried cell through a side arm. After evacuation, the cell was sealed and placed in a resistance furnace. The observation of the droplets of liquid on the windows was accomplished conveniently by means of a beam of light passing through the cell and a lens or microscope focused on the condensing surface of the window. Thus the temperature at which the droplets disappeared was easily observable.

**Hydrogen–Hydrogen Halide Mixtures.**—Iron cylinders two feet in length were evacuated to remove air and moisture and attached to a reservoir of liquid, anhydrous hydrogen halide, contained in a small heavy copper cylinder designed to withstand high pressures. The hydrogen halide was introduced and the pressure regulated by the control of the liquid temperature. Hydrogen was then introduced from a cylinder at a higher pressure, the two cylinders coming to the same total pressure which was measurable. After being introduced into the cylinder, the two gases were allowed to stand for several days to ensure thorough mixing.

**Apparatus.**—The partial pressure of cuprous chloride over copper metal in the presence of hydrogen–hydrogen chloride mixtures was determined with an apparatus somewhat similar to that used by Biltz, Fischer and Juza.<sup>6</sup> Temperature control (to  $\pm 1^\circ$  in the furnace manufactured by the Burrell Company) was accomplished by means of a "Micromax Indicating Controller," using chromel–alumel thermocouples in conjunction with a potential bucking device to extend the operating range of the instrument. Temperature measurement was achieved with a relative uncertainty of three degrees but an absolute uncertainty of

(6) W. Biltz, W. Fischer and R. Juza, *Z. anorg. allgem. Chem.*, **176**, 121 (1928).

five degrees through use of chromel-alumel thermocouples checked against a calibrated platinum-platinum rhodium couple. In Fig. 1 is shown the interior of the furnace chamber with the clear quartz tube designed to facilitate ease of removal of the condensed vapors. The pressure control device consisted of a mercury manometer fitted with tungsten electrodes attached after the hydrogen chloride absorber. Pressures either greater or less than the set value would activate relays which in turn activated solenoid valves arranged to add or withdraw small amounts of gas from the reservoir behind the absorber. This arrangement was capable of maintaining automatically any pressure between two tenths and one atm. to within 1 mm. of the desired value.

**Analysis.**—Gas analysis was performed in a sampling bulb of known volume into which the hydrogen-hydrogen halide mixture was introduced at known pressure and temperature. Water added to this bulb would extract the acid which was titrated by standardized base. With this information, calculation of the pressure of hydrogen chloride was possible, the pressure of hydrogen then being acquired by difference.

The usual procedure for copper analysis was used.

**Procedure.**—During each heating up period hydrogen was passed through the copper in a reverse direction thus ridding the metal of any contaminating oxide or residual halide. As the desired temperature was reached, the whole system was evacuated and the reaction mixture introduced in a direction opposite from the normal flow direction. A particular mixture, stored at a high pressure in an iron cylinder fitted with a needle valve to reduce the pressure, was used for several values of the ratio ( $P_{\text{HCl}}/P_{\text{H}_2}^{1/2}$ ). Variation in this ratio was achieved through changes in the total pressure of hydrogen-hydrogen chloride allowed to pass through the apparatus. At the instant the pressure to be maintained throughout the experiment was reached, the flow was caused to pass in the normal direction and introduced into the absorption tube. The amount of acid collected in the absorption solution then was a measure of the exact volume of gas passed through the chamber inasmuch as the relative pressures of hydrogen and hydrogen chloride had been previously secured. A flow rate between twenty and thirty cc. per minute was usually used for each determination which required from two to four hours of flow.

**Diffusion Errors.**—Under conditions of condensations where large concentration gradients were set up as a result of precipitation of the vapor, considerable diffusion of the condensable gas occurred. The existence of such an error in a particular experiment could be recognized by the pattern of the condensation. For example, if the first small decrease in temperature as the gas leaves the chamber causes saturation of the vapor and subsequent condensation, obviously there can be little diffusion. However, should the gas pass several cm. into the temperature gradient before saturation and condensation occur, diffusion of the condensable vapor is probably taking place. With partial pressures of halide less than  $10^{-3}$  atm. the former type condensation occurred producing small metallic copper crystals, beginning immediately after the gas left the copper chamber, whereas at higher pressures condensation of the second type with formation of solid or liquid halide far along the tube began to be of importance. Experiments conducted under the latter conditions with considerable diffusion error gave results which unmistakably checked the general conclusions of this report, namely, that there exists a higher polymer than dimer, although for quantitative calculations the data were not used. However, for the reason already stated and for the additional reason that experiments 24–29 performed at flow rates varying from 20 to 90 cc./sec. showed no significant flow rate dependency, the data employed in the calculations of this report were assumed subject to negligible diffusion error.

The possibility of a thermal diffusion effect causing separation of the hydrogen-hydrogen chloride mixture was also considered. Calculations based on theoretical con-

siderations which may not be adequately developed here but will be presented at a later time, showed that any separation in the reaction zone would be quite small.

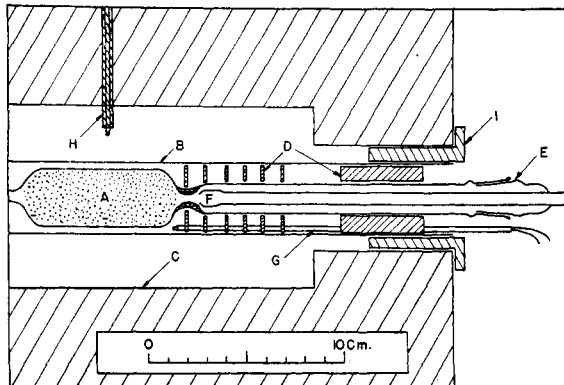


Fig. 1.—High temperature chamber: A, metallic copper in quartz tube; B, protective quartz tube; C, Burrell furnace; D, asbestos baffles and insulation; E, ground joints; F, ground joints; G, thermocouple; H, thermocouple for micromax controller; I, refractory spacer.

## Calculations and Results

**Pressure Ratio, ( $P_{\text{HCl}}/P_{\text{H}_2}^{1/2}$ )**—For each tank of the gaseous mixture there was a constant mole fraction ratio,  $N_{\text{HCl}}/N_{\text{H}_2}$ , which has been termed  $\alpha$ , and this must be constant at whatever pressure the gas is withdrawn. Since  $N_{\text{HCl}} = 1 - N_{\text{H}_2} = \alpha/(1 + \alpha)$ , then the desired ratio in terms of  $\alpha$  is

$$(P_{\text{HCl}}/P_{\text{H}_2}^{1/2}) = \frac{N_{\text{HCl}} P^{1/2}}{N_{\text{H}_2}^{1/2}} = \frac{\alpha \sqrt{P}}{\sqrt{\alpha + 1}} \quad (2)$$

where  $P$  represents the total pressure of hydrogen and hydrogen chloride. As is apparent from this expression, the pressure ratio will remain constant if the pressure is constant, except when reaction (1) causes a shift in the composition ratio,  $\alpha$ . Employing the substitution  $\beta = \alpha^2/(\alpha + 1)$ , one can find by a simple derivation that the correction for change in  $\beta$  is proportional to the mole fraction of cuprous halide in the gas.

$$\beta = \beta^0 - [(\alpha^2/2 + 2\alpha)]N_{\text{Cu}} \quad (3)$$

In equation (3)  $\beta^0$  represents the quantity  $\alpha^2/(\alpha + 1)$  before interaction of the copper and hydrogen chloride,  $\beta$  the same quantity after equilibrium has been attained, and  $N_{\text{Cu}}$  is the mole fraction of cuprous halide in moles of copper in vapor per total moles of gas. The detailed derivation of equation 3 is

$$\begin{aligned} N_{\text{HCl}} &= N_{\text{HCl}}^0 - N_{\text{Cu}} \\ N_{\text{H}_2} &= N_{\text{H}_2}^0 + 1/2 N_{\text{Cu}} \end{aligned}$$

This assumes no change in the total number of moles when reaction (1) takes place, which is satisfactory since the largest partial pressure of Cu halide in any of the runs was  $3.8 \times 10^{-4}$  atm. compared to a total pressure of 0.557 atm.

$$\beta = \frac{N_{\text{HCl}}^2}{N_{\text{H}_2}} = \frac{(N_{\text{HCl}}^0 - N_{\text{Cu}})^2}{(N_{\text{H}_2}^0 + \frac{1}{2}N_{\text{Cu}})} = \frac{(N_{\text{HCl}}^0)^2 (1 - 2N_{\text{Cu}}/N_{\text{HCl}}^0)}{N_{\text{H}_2}^0 (1 + \frac{1}{2}N_{\text{Cu}}/N_{\text{H}_2}^0)}$$

This step neglects  $N_{\text{Cu}}^2$  with respect to  $2N_{\text{Cu}}$ .  $N_{\text{HCl}}^0$  since for the largest Cu halide mole fraction, the first term is  $4.7 \times 10^{-7}$  compared to  $3 \times 10^{-4}$ .

$$\beta = \frac{(N_{\text{HCl}}^0)^2}{N_{\text{H}_2}^0} [1 - 2N_{\text{Cu}}/N_{\text{HCl}}^0 - \frac{1}{2}N_{\text{Cu}}/N_{\text{H}_2}^0]$$

This step neglects higher powers of  $N_{\text{Cu}}/N_{\text{H}_2}^0$  with respect to the first power which is reasonable since the ratio is  $9 \times 10^{-4}$  in the case of largest Cu halide mole fraction.

$$\beta = \beta^0 - N_{\text{Cu}} [2N_{\text{HCl}}^0/N_{\text{H}_2}^0 + \frac{1}{2}(N_{\text{HCl}}^0/N_{\text{H}_2}^0)^2]$$

$$\beta = \beta^0 - N_{\text{Cu}} [2\alpha + \frac{1}{2}\alpha^2]$$

This applies for all gaseous species that may be present. In Table I are given the results of these calculations for the cuprous chloride system based on experimental values for  $\beta^0$ , 0.1945 in experiments 24-36 and 0.0290 in 37-43. Table V for cuprous bromide is based on  $\beta^0 = 0.001938$ .

**Pressure of Cuprous Chloride.**—The entries into column four of Table I were calculated from equation (4) which requires the number of moles of cuprous chloride volatilized,  $n_{\text{Cu}}$ , the quantity of hydrogen chloride passed over into the absorber,  $n_{\text{HCl}}$ , and the mole ratio,  $\alpha$ .

$$P_{\text{CuCl}} = \left[ \frac{n_{\text{Cu}}}{n_{\text{(total)}}} \right] P_{\text{(total)}} = \frac{n_{\text{Cu}}}{n_{\text{HCl}}} \left( \frac{\alpha}{1 + \alpha} \right) P \quad (4)$$

TABLE I

VOLATILITY OF GASEOUS CUPROUS CHLORIDE OVER COPPER METAL IN HYDROGEN-HYDROGEN CHLORIDE MIXTURES

Expt.	Temp., °K.	$P$ (total), atm.	$P_{\text{CuCl}}$ , atm.	$P_{\text{HCl}}/P_{\text{H}_2}^{1/2}$
24	988	0.828	$1.728 \times 10^{-4}$	0.401
27	988	.824	1.482	.392
28	988	.824	1.63	.401
29	988	.828	1.72	.400
31	1226	.916	4.16	.420
33	1226	.601	2.35	.341
43	1268	.859	0.833	.1584
34	1309	.962	6.63	.432
35	1309	.557	3.815	.328
36	1309	.203	1.538	.198
37	1309	.967	1.368	.163
38	1309	.745	1.18	.147
39	1309	.452	0.87	.114
40	1309	.1804	0.509	.0722
41	1309	.345	0.693	.0999
42	1340	.849	1.740	.1568

Column four represents not the actual partial pressure of cuprous halide since the degree of association is not known, but rather what the pressure would be if all species were dissociated to monomeric, cuprous chloride gas.

**Chlorine to Copper Ratio in the Polymer.**—Volatilization of two weighed samples of cuprous chloride mixed with a small amount of metallic

copper at 850-900°K. and at a pressure of  $10^{-2}$ - $10^{-3}$  mm. allowed analysis of g. of copper per g. of vapor. After the calculation of chloride by difference, the ratios Cl/Cu = 0.97 and Cl/Cu = 1.08 subsequently were obtained. This justifies the polymer molecule represented in reaction (1).

**Establishment of the Vapor Species and Calculation of Equilibrium Constants.**—The cuprous chloride vapor in the hydrogen-hydrogen chloride system undoubtedly is composed of two or more species, each of which may be represented in terms of its equilibrium constant  $K$  and the pressure ratio ( $P_{\text{HCl}}/P_{\text{H}_2}^{1/2}$ ).

$$P'_{\text{CuCl}} = K_1 (P_{\text{HCl}}/P_{\text{H}_2}^{1/2}) + K_2 (P_{\text{HCl}}/P_{\text{H}_2}^{1/2})^2 + K_3 (P_{\text{HCl}}/P_{\text{H}_2}^{1/2})^3 \quad (5)$$

Whereas  $P'_{\text{CuCl}}$  represents the actual partial pressure of cuprous halide in the vapor state, the quantity measurable by the procedure employed in this paper is rather

$$P_{\text{CuCl}} = K_1 (P_{\text{HCl}}/P_{\text{H}_2}^{1/2}) + 2K_2 (P_{\text{HCl}}/P_{\text{H}_2}^{1/2})^2 + 3K_3 (P_{\text{HCl}}/P_{\text{H}_2}^{1/2})^3 \quad (6)$$

where each  $K$  is the equilibrium constant for reaction (1) after insertion of the proper  $X$  value. Other calculations described in the next paragraphs justified the elimination of higher polymers than the trimer.

At any one temperature where three or more experimental volatilities were available, for example at 1309°K., a simultaneous solution of equation (6) was possible. This solution was attained by means of a least squares method assuming the same percentage error in each of the  $P_{\text{CuCl}}$  terms. The constants arising from the calculations at 1309°K. were  $K_1 = 7.12 \cdot 10^{-4}$ ,  $2K_2 = -3.7 \cdot 10^{-4}$ , and  $3K_3 = 50 \cdot 10^{-4}$ , indicating a negative quantity for  $K_2$ . Inasmuch as this difference from zero is of the order of the maximum error to be expected from the experimental uncertainty, this result was taken as proof of the non-existence of dimeric cuprous chloride. This conclusion was confirmed by additional evidence shown in a following paragraph. With  $K_2 = 0$  recalculation of the constants yields by a least mean squares procedure  $K_1 = 6.83 \cdot 10^{-4}$  and  $3K_3 = 43.1 \cdot 10^{-4}$ . Although insufficient data were available at other temperatures to duplicate the calculation to eliminate the possible existence of dimeric halide, enough were obtained at 1226°K. to arrive at a solution for monomer and trimer constants,  $K_1 = 1.93 \cdot 10^{-4}$  and  $3K_3 = 45.2 \cdot 10^{-4}$ . In Table II are summarized the equilibrium constants derived in the foregoing manner unless otherwise noted.

A more obvious evaluation of the formula of polymer was secured from the data at 1226°K. and 1309°K. by subtracting from the total  $P_{\text{CuCl}}$  of Table I the partial pressure of monomer calculated with the  $K_1$ 's from Table II. This is justified by the fact that at 1226°K. in the region of high  $[(\text{HCl})/(\text{H}_2)^{1/2}]$  the monomer is a minor

TABLE II

EQUILIBRIUM CONSTANTS FOR REACTION (1)					
$T, ^\circ\text{K.}$	$1/T \times 10^4$	$K_1 \times 10^4$	$3K_1 \times 10^4$	$\log K_1$	$\log 3K_1$
988	10.12	(0.024) <sup>b</sup>	25.9	(-5.63) <sup>b</sup>	-2.587
1226	8.16	1.93(±0.02) <sup>a</sup>	45.2(±0.2) <sup>a</sup>	-3.715	-2.345
1268	7.89	4.17	(44) <sup>b</sup>	-3.380	(-2.36) <sup>b</sup>
1309	7.64	6.84(±0.16) <sup>b</sup>	43.1(±4.0) <sup>a</sup>	-3.166	-2.366
1340	7.46	9.62	(48) <sup>b</sup>	-3.017	(-2.32) <sup>b</sup>

<sup>a</sup> These values are the result of the least squares solution of the data at the temperature indicated. The mean least square errors are also shown to indicate the precision of the constants although the actual uncertainty due to experimental errors is 5% in the case of  $K_1$  and 10% in the case of  $K_3$ . <sup>b</sup> Values calculated by interpolation or extrapolation of experimentally determined constants assuming a linear relation between  $\log K$  and  $1/T$  over the temperature range employed.

species and that at 1309°K. the monomer constant has been well defined by data collected under conditions where the monomer was the major species. Equation (6) was modified to give

$$P_{\text{CuCl}} - K_1(P_{\text{HCl}}/P_{\text{H}_2}^{1/2}) = X \cdot P_{\text{Cu}_3\text{Cl}_3} = X \cdot K_2 [P_{\text{HCl}}/P_{\text{H}_2}^{1/2}]^2$$

the log of which gave

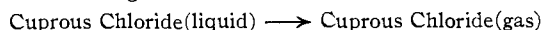
$$\log(X \cdot P_{\text{Cu}_3\text{Cl}_3}) = X \log(P_{\text{HCl}}/P_{\text{H}_2}^{1/2}) + \text{constant} \quad (7)$$

Thus the slope of a plot of  $\log(X \cdot P_{\text{Cu}_3\text{Cl}_3})$  versus  $\log(P_{\text{HCl}}/P_{\text{H}_2}^{1/2})$  would be the polymer number  $X$ . In Fig. 2 these results are shown (including a point at 1309°K. in error because of an inaccurate analysis) with slopes both at 1226°K. and 1309°K. of 3.09.

**Calculation of Molecular Weight.**—This determination was intended to verify the results of the preceding section, which indicate the existence of a trimeric molecule at low temperatures. Therefore, at a lower temperature than that used by Wartenberg and Bosse,<sup>2</sup> Meyer and Meyer,<sup>3</sup> and Biltz and Meyer,<sup>4</sup> the molecular weight was re-evaluated, but by a different procedure. Inasmuch as the partial pressure of vapor over liquid cuprous chloride has been quite well established by Maier,<sup>7</sup> Tarasenkov and Kozhmyakov<sup>8</sup> and Wartenberg and Bosse,<sup>2</sup> a measure of the density of copper in the vapor would allow calculation of the molecular weight. An analysis of their data yielded, through the plotting of

$$\Sigma = -4.575 \log P + 2.303 \Delta C_p \log T, \text{ versus } 1/T$$

the following results for the reaction



$$\Delta C_p = -16(\text{assumed})$$

$$\Delta F = 37,870 + 36.85T \log T - 140.82T \quad (8)$$

$$\Delta H = 37,870 - 16T \quad (9)$$

$$\Delta S = 124.82 - 36.85 \log T \quad (10)$$

Thus at the temperature of this experiment, 1119°K. ± 5°, the vapor pressure is calculated to be 0.0668 atm. (±0.008) from equation (8) and the relation  $\log P = -\Delta F/2.303RT$ . The uncertainty is the sum of the average deviation of the vapor pressure data from equation (8) and the possible deviation as a consequence of a 5° uncertainty in the temperature of the experi-

(7) C. G. Maier, Bureau of Mines T. P. 360 (1929).

(8) P. N. Tarasenkov and P. A. Kozhmyakov, *J. Gen. Chem.*, (U. S. S. R.), **5**, 830 (1935).

ments to be described subsequently. Two separate experimental determinations of the volatility of liquid cuprous chloride at 1119°K. with temperature uncertainties of five and ten degrees, respectively, gave 212 and 171 mg. of cuprous chloride. The volumes of carrier gas were 265.0 and 187.7 cc. over water at 297.2° and 299.6°K., respectively. Through use of the equation, molecular weight =  $(g. \text{CuCl})RT/PV$ , the values  $300 \pm 36$  and  $341 \pm 55$  were obtained, which correspond to the theoretical value 297 for the trimeric molecule,  $\text{Cu}_3\text{Cl}_3$ .

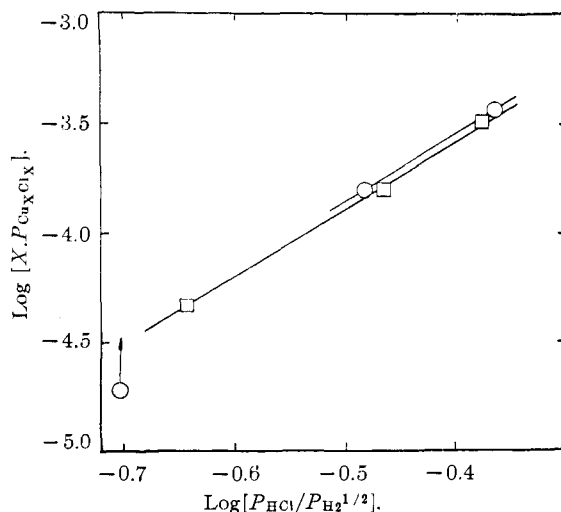


Fig. 2.—Polymer number of cuprous chloride complex vapor molecule: the data, O, 1309°K. and □, 1226°K., give for the slope  $X = 3.09$ .

Likewise, a value for the molecular weight was obtained from the quartz sealed cell experiment in which the temperature of condensation of a known weight of cuprous chloride was determined. A 11.24 mg. sample of cuprous chloride in a 49.1 cc. quartz cell at an average temperature of 1197°K. was completely vapor at or above a window temperature of 1141°K. ± 5°. This information together with a vapor pressure at 1141°K. calculated to be 0.0824 atm. from equation (8) was sufficient to obtain a molecular weight of  $283 \pm 34$ .

**Heat of Formation of  $\text{CuCl(g)}$ .**—From the variation of the equilibrium constant,  $K_1$ , with

temperature the heat of formation of gaseous monomer from copper metal and hydrogen chloride is calculable. Through use of the  $\Sigma$  function,  $\Sigma = -4.575 \log K - 4.17 \log T$ , tabulated in Table III,  $\Delta H_0$  was gotten as the slope of the  $\Sigma$

TABLE III

$\Sigma$ FUNCTION FOR REACTION: $\text{Cu(s)} + \text{HCl} = \text{CuCl(g)} + \frac{1}{2}\text{H}_2$				
$T, ^\circ\text{K.}$	$1/T$	$\frac{-4.575}{\log K}$	$-4.17 \log T$	$\Sigma$
1226	$8.16 \times 10^{-4}$	17.00	-12.877	4.12
1268	7.89	15.46	-12.939	2.52
1309	7.64	14.48	-12.994	1.49
1340	7.46	13.80	-13.038	0.76

versus  $1/T$  plot shown in Fig. 3. The  $\Delta C_p = -1.81$  was inserted in order to improve the extrapolation properties of the equation, and was calculated assuming  $C_p(\text{CuCl}) = 8.80$ ,  $C_p(\frac{1}{2}\text{H}_2) = 3.73$ ,  $C_p(\text{HCl}) = 7.84$  and  $C_p(\text{Cu}) = 6.50$ .

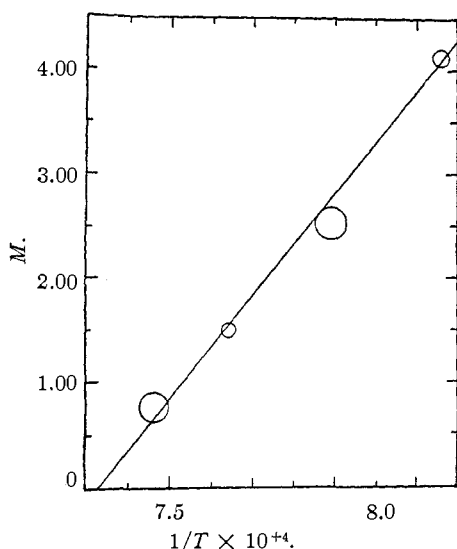
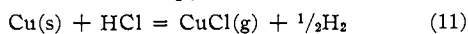


Fig. 3.— $\Sigma$  Plot for determination of heat of reaction ( $\Delta H_0$ ) for  $\text{Cu(s)} + \text{HCl(g)} = \text{CuCl(g)} + \frac{1}{2}\text{H}_2(\text{g})$ .

From Fig. 3, with the uncertainties indicated by means of the circle radii,  $\Delta H_0$  is found to be  $49.32 \pm 4$  kcal., which gives equations of free energy, heat and entropy of reaction



$$\Delta F = 49,320 + 4.17T \log T - 36.15T \quad (12)$$

$$\Delta H = 49,320 - 1.81T \quad (13)$$

$$\Delta S = 34.34 - 4.17 \log T \quad (14)$$

Through use of the entropy of reaction (11) given by equation (14) and the entropies of copper, hydrogen chloride and hydrogen at  $1300^\circ\text{K.}$  as given by Brewer<sup>9,10</sup> ( $S_{\text{Cu}} = 17.28$ ,  $S_{\text{HCl}} = 55.29$ , and  $S_{\text{H}_2} = 41.68$  e. u.) the entropy of the

(9) L. Brewer "The Thermodynamic Properties of Common Gases," National Nuclear Energy Series, Vol. 19B, paper 5, 1949, McGraw-Hill Book Co., New York, N. Y.

(10) L. Brewer, "The Thermodynamic and Physical Properties of the Elements," National Nuclear Energy Series, Vol. 19B, paper 3.

gaseous molecule,  $\text{CuCl}$ , was calculated to be  $73.8 \pm 4$  e. u. at  $1300^\circ\text{K.}$

An alternate calculation of the entropy of the diatomic molecule, using spectroscopic data by Ritschl<sup>11</sup> who gives  $\omega_0 = 415.3 \text{ cm.}^{-1}$  and also using an estimate of interatomic distance by Stevenson<sup>12</sup> who gives  $d = (2.00 \pm 0.05) 10^{-8} \text{ cm.}$ , produces a value of  $69.6 \pm 0.5$  e. u. The uncertainty indicated in the final result arises from the application of a  $0.15 \cdot 10^{-8} \text{ cm.}$  uncertainty to the interatomic distance to allow for a possible variation of  $d$ . Kelley<sup>13</sup> gives the equations required for the calculation.

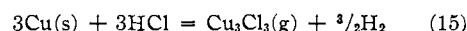
It is thus apparent that the indicated slope of the  $\Sigma$  function plot in Fig. 3 may be in error by approximately 6 kcal. The attributing of such an error to a diffusion effect would be difficult since this would produce a deviation in an opposite direction, if one assumes greater diffusion at increasing temperatures. The probable answer is that the error limits attached to the data may be somewhat smaller than the actual uncertainties, although the results on Fig. 3 seem to signify otherwise. Nevertheless, revision of the thermodynamic equations, to give the observed free energy of reaction and the calculated entropy, results in the equations

$$\Delta F = 43,660 + 4.17T \log T - 31.81T \quad (12')$$

$$\Delta H = 43,660 - 1.81T \quad (13')$$

$$\Delta S = 30.0 - 4.17 \log T \quad (14')$$

**Heat of Formation of  $\text{Cu}_3\text{Cl}_3(\text{g})$ .**—Because of the uncertainty of the  $\Delta C_p$  for the reaction and the apparent inaccuracies in the data  $\Delta H$  was evaluated as the slope of the  $\log K$  versus  $1/T$  function. For the reaction



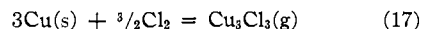
in the neighborhood of  $1300^\circ\text{K.}$ , we find the results

$$\Delta F = 4500 + 9.4T \quad (16)$$

$$\Delta H = 4500 \pm 2000 \text{ (calories)}$$

$$\Delta S = -9.4 \pm 3 \text{ e. u.}$$

Confirmation of trimer thermodynamic constants can be achieved by calculation of the heat of formation of the gaseous trimer molecule from the elements. From the heat of reaction (15)  $\Delta H = 4.5 \pm 2$  kcal. and the heat of formation of hydrogen chloride at  $1300^\circ\text{K.}$ ,  $-22.53$  kcal., from Brewer,<sup>9</sup> the heat of reaction (17)



is found to be  $-63.1 \pm 2$  kcal. The heat of formation of cuprous chloride liquid,  $\Delta H_{1300^\circ\text{K.}} = -26.6 \pm 3$  kcal., has been evaluated by Brewer, Bromley, Gilles and Lofgren<sup>14</sup> from the heat of formation of solid cuprous chloride,  $\Delta H_{298} = -32.6 \pm 0.4$  kcal., and estimated heat capacities

(11) R. Ritschl, *Z. Physik*, **42**, 172 (1927).

(12) D. P. Stevenson, *J. Chem. Phys.*, **8**, 898 (1940).

(13) K. K. Kelley, Bureau of Mines Bulletin, No. 434 (1941).

(14) L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, "The Thermodynamic Properties of the Halides," National Nuclear Energy Series, Vol. 19B, paper 6.

of the solid and liquid states, and the estimated entropy of fusion of the solid. From this value and the heat of vaporization at 1300°K. of liquid of the polymer given by equation (9), an alternate heat of formation of the trimer,  $\Delta H_{1300} = -62.7 \pm 9$  kcal., is acquired which corresponds to  $-63.1 (\pm 2)$  kcal. from experiment.

**Cuprous Bromide Equilibrium Constants.**—In Table IV are given the data arising from a short series of experiments with hydrogen-hydrogen bromide mixtures over copper metal. Insufficient data were collected to establish the gaseous species, nevertheless there seems to be some qualitative similarity between the  $P_{\text{CuBr}}$  versus  $(P_{\text{HBr}}/P_{\text{H}_2}^{1/2})$  relations of this system and that of the cuprous chloride system. At two experimental temperatures, 1323°K. and 1351°K., the equilibrium constants were evaluated assuming monomer and trimer. In this case the values of  $K_1$  were  $7.17 \cdot 10^{-3}$  and  $8.4 \cdot 10^{-3}$  and the value of  $3K_3$  was 1.45, assumed constant at the two temperatures.

TABLE IV

VOLATILITY OF CUPROUS BROMIDE OVER COPPER METAL IN HYDROGEN-HYDROGEN BROMIDE MIXTURES

Expt.	T, °K.	P (total), atm.	$P_{\text{CuBr}}$ , atm.	$P_{\text{HBr}}/P_{\text{H}_2}^{1/2}$
45	1323	0.2956	$1.900 \times 10^{-4}$	0.02355
47	1323	.5165	$2.635 \times 10^{-4}$	.03125
48	1323	.7623	$3.507 \times 10^{-4}$	.0380
49	1323	.964	$4.24 \times 10^{-4}$	.0428
50	1351	.1998	$1.724 \times 10^{-4}$	.01930

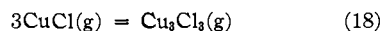
Column four represents not the actual partial pressure of cuprous halides since the degree of association is not known, but rather indicates what the pressure would be if all species were dissociated to monomeric, cuprous bromide gas.

Cuprous bromide vapor pressure measurements by Jellinek and Rudat<sup>15</sup> when used in conjunction with data by Wartenberg and Bosse<sup>2</sup> indicate a molecular weight approximately that of a dimer. The electron diffraction results of Maxwell and Mosley<sup>5</sup> would indicate the presence of trimer since they obtain very similar patterns for the chloride and bromide systems. The presence of a considerable amount of trimer is also indicated by the fact that the molecular weight obtained from the data of Jellinek and Rudat is about thirty units above that for a dimer. However, if one assumes only monomer and trimer one would obtain a molecular weight considerably higher than that obtained by Jellinek and Rudat. Thus, one would have to assume the presence of monomer, dimer and trimer in the cuprous bromide system to reconcile all the data. The vapor pressure data at their face value would indicate two per cent. monomer, 78 mole per cent. dimer, and 20 mole per cent. trimer. However, some of the data may be in error and further experiments would be necessary to definitely fix the species present.

(15) K. Jellinek and A. Rudat, *Z. physik. Chem.*, **A143**, 55 (1929).

## Discussion

**Monomer-Trimer Equilibrium.**—Through use of the equilibrium results for these two species the equilibrium constant for the reaction



can easily be evaluated. Equations (12') and (16) yield for the free energy of reaction (18)

$$\Delta F = -126,400 - 12.51T \log T + 104.7T \quad (19)$$

Thus at low temperatures the equilibrium will be shifted to favor formation of the trimer, whereas at high temperatures the monomer becomes the species of importance. This was demonstrated by calculation of the vapor composition existing at various temperatures and is summarized in Table V. It is quite apparent that at a temperature in the neighborhood of 1750°K., the region investigated by Wartenberg and Bosse,<sup>2</sup> Meyer and Meyer,<sup>3</sup> and Biltz and Meyer<sup>4</sup> in their vapor density measurements, the average molecular weight of the species would approximate that of a dimeric molecule. By coincidence, then, under special conditions the experimental average molecular weight could coincide with that of the dimer.

TABLE V

DISSOCIATION OF GASEOUS CUPROUS CHLORIDE POLYMER AT HIGH TEMPERATURES:  $\text{Cu}_3\text{Cl}_3(g) = 3\text{CuCl}(g)$

T, °K.	P, atm.	K	Mole % CuCl	Mole % $\text{Cu}_3\text{Cl}_3$
1000	0.0218 <sup>a</sup>	$1.15 \times 10^{-13}$	0.0014	100.0
1632 (b. p.)	1.00 <sup>a</sup>	$1.495 \times 10^{-3}$	11.0	89.0
1750	1.00	$1.79 \times 10^{-2}$	23.9	76.1
2000	1.00	1.11	69.6	30.4

<sup>a</sup> Saturated vapor.

TABLE VI<sup>16</sup>

VAPORIZATION OF CUPROUS AND SILVER HALIDES TO MONOMERIC GAS AT 1300°K.  $\text{MX}(l) = \text{MX}(g)$

MX	$\Delta F_{1300^\circ\text{K.}}$ , kcal.	$\Delta H_{1300^\circ\text{K.}}$ , kcal.	$\Delta S_{1300^\circ\text{K.}}$ , e. u.
CuCl	15.8(±3)	46.5(±7)	23.6(±5)
CuBr	13.5(±3)	45.1(±7)	24.3(±5)
CuI	> 3.9	> 39.0	27.0(±5)
AgCl	12.9(±1)	43.4(±3)	23.5(±1)
AgBr	10.5(±1)	40.8(±3)	23.3(±2)
AgI	9.8(±1)	39.8(±3)	23.1(±2)

(16) References to Table VI: Free Energies of Vaporization.—For CuCl and CuBr the equilibrium data of equation (12') and Table IV were employed to obtain the  $\Delta F$  of formation of the gaseous molecules and the Halide Report, by Brewer, *et al.*,<sup>14</sup> was used to obtain the  $\Delta F$  of formation of the liquid at 1300°K. For CuI (see section iodide polymer) vapor pressures by Jellinek and Rudat<sup>15</sup> and Wartenberg and Bosse<sup>3</sup> give an uncertain value for  $\Delta F_v$ . For AgCl, AgBr and AgI, Maier<sup>7</sup> Von Wartenberg and Bosse,<sup>2</sup> Jellinek and Rudat<sup>15</sup> give vapor pressures which are presented by Kelley.<sup>1</sup> Entropies of Vaporization.—Entropies of the gaseous molecules were calculated by means of the Sackur-Tetrode equation, through use of spectroscopic data tabulated by Herzberg<sup>17</sup> and Stevenson's<sup>12</sup> interatomic distances. Entropies of the liquids at 1300°K. were procured from the Halide Report by Brewer<sup>14</sup> from which the  $\Delta S_v$  was acquired by difference. Heats of Vaporization.—The relation  $\Delta H = \Delta F + T\Delta S$  was employed.

(17) G. Herzberg, "Diatomic Molecules," Prentice Hall, New York, N. Y., 1939.

**Thermodynamics of Vaporization to Monomeric Halides.**—Sufficient information was available in addition to the data of this report to summarize the thermodynamic constants of the vaporization reaction  $\text{MX}(l) = \text{MX}(g)$ . In view of the similarity of cuprous and silver halides, both were included in the summary calculations shown in Table VI. The uncertainty indicated for each value is the square root of the sum of the squares of the probable errors of all quantities employed in yielding the results shown. As an aid in understanding the origin of each quantity presented, a footnote has been included.

**Dissociation Energies of Monomeric Halides.**—From available spectroscopic data, the calculation of the dissociation energies of the diatomic molecules of cuprous and silver halides has been possible through the linear Birge-Sponer extrapolation of vibrational states (L. B. X.). These are summarized both by Herzberg<sup>17</sup> and Gaydon<sup>18</sup> and are included in column three of Table VII with the number of vibrational states measured. At the same time, by means of the  $\Delta F$  of formation of the gaseous molecules from  $\text{H}_2$ -HX equilibrium data in the cases of cuprous chloride and cuprous bromide and vapor pressure in the case of cuprous iodide and the silver halides, calculation of  $\Delta H_0$  was possible. In this calculation,  $\Delta F - \Delta H_0$  values from Brewer<sup>9,10</sup> and Brewer, Bromley, Gilles and Lofgren<sup>14</sup> were required. These thermochemical calculations (T.C.) are summarized in column two of Table VII. Since the accuracy of the  $D_0$  values depends upon the accuracy of the heat of vaporization of the metals, a survey was made of the original data given by Baur and Brunner,<sup>19</sup> Marshall, Dornte and Norton<sup>20</sup> and in the references given by Kelley<sup>1</sup> for the vapor pressures of copper and silver. The best values that can be given are  $\Delta H_0^0 = 82 \pm 5$  kcal. for the sublimation of copper at 0°K. and  $\Delta H_0^0 = 70 \pm 3$  kcal. for the sublimation of silver. It might be noted that the recent apparently reliable measurements of Baur and Brunner<sup>19</sup> on copper and silver give  $\Delta H_0^0$  values about 8 kcal. lower than the values given above. Until this discrepancy is resolved, the reliability of the values used is questionable.

**Polymer in the Cuprous Iodide System.**—At the temperature of the vapor pressure determinations by Von Wartenberg and Bosse<sup>2</sup> calculations have shown that a considerable partial pressure of monatomic iodine is present. The maximum possible pressure of monomer, that obtained after subtraction of the iodine partial pressure, was employed in the calculations for Tables VI and VII, where the free energy of

vaporization to monomer was desired. However, the existence of any polymer would decrease the monomer pressure. The view that this condition actually exists is substantiated by vapor pressure measurements over cuprous iodide conducted by Jellinek and Rudat<sup>15</sup> in which the weight of halide in the vapor was determined. Application of the data of Von Wartenberg and Bosse<sup>2</sup> after subtraction of the iodine partial pressure indicates a vapor of average molecular weight, 218, compared with a theoretical value of 190 for monomer. This quite definitely indicates polymerization in the vapor inasmuch as the experimental errors probably occurring in these experiments, namely, oxidation of iodide to iodine, would decrease the observed molecular weight. Also, Maxwell and Mosley<sup>5</sup> obtained electron diffraction results for cuprous chloride vapor which were similar to those for the chloride and bromide systems and which could be consistent with a cyclic trimer structure.

TABLE VII  
DISSOCIATION ENERGIES, ELECTRON VOLTS  
 $\text{MX}(g) = \text{M}(g) + \text{X}(g)$

<i>MX</i>	$D_0$ (T. C.)	$D_0$ (L. B. X.)
CuCl	3.82 ( $\pm 0.25$ )	3.3 (0-11)
CuBr	3.43 ( $\pm 0.25$ )	3.5 (0-9)
CuI	<3.27	3.0 (0-15) <sup>a</sup>
AgCl	3.31 ( $\pm 0.2$ )	3.11 (0-9)
AgBr	3.05 ( $\pm 0.4$ )	2.77 (0-15)
AgI	2.66 ( $\pm 0.4$ )	3.0 (0-17)

<sup>a</sup> Probably in error because of ionic forces.

**Structure of the Trimer Molecule.**—The electron diffraction results by Maxwell and Mosley<sup>5</sup> indicate that at least two interatomic distances occur in the molecule, disclosing a non-linear structure. From the fact that a dimeric molecule is apparently non-existent, a chain structure does not at first seem to be the most logical configuration. In view of the unusual stability and low entropy of vaporization of the trimer its structure may be cyclic, as is benzene, with alternate copper and halogen atoms.

### Summary

1. The existence of a trimeric molecule  $\text{Cu}_3\text{Cl}_3$  in cuprous chloride vapors was disclosed as a result of measurements of volatility of cuprous chloride in hydrogen-hydrogen chloride mixtures over copper metal. This conclusion was verified by vapor density measurements at 1119°K. with pure cuprous chloride. At the boiling point of liquid cuprous chloride, 1632°K. at 1 atm., the monomeric CuCl partial pressure is only 11% and no evidence was found for  $\text{Cu}_2\text{Cl}_2$ .

2. In the cuprous bromide and iodide systems evidence was found for the existence of polymer molecules in the vapor, but the actual polymer was not evaluated.

3. The heats of formation of the various species

(18) A. G. Gaydon, "Dissociation Energies," Chapman and Hall, Ltd., London, 1947.

(19) E. Baur and R. Brunner, *Helv. Chim. Acta*, **17**, 958 (1934).

(20) A. L. Marshall, R. W. Dornte and F. J. Norton, *THIS JOURNAL*, **59**, 1161 (1937).

