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THE THERMODYNAMICS OF GASEOUS, CUPROUS
CHLORIDE MONOMER AND TRIMER.

By

Leo Brewer and Norman L. Lofgren

January 2, 1948

Berkeley, California

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ABSTRACT

1. The existence of a trimeric molecule, Cu_3Cl_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 partial pressure is only 11%.
2. In the cuprous bromide and iodide systems evidence was found for the existence of polymer molecules in the vapor, but the actual polymer number was not evaluated.
3. The heats of formation of the various species at 1300°K and under standard conditions from the elements were found to be: CuCl(g) , $\Delta H_{1300^\circ\text{K}} = 18.8 \pm 4$ kcal; $\text{Cu}_3\text{Cl}_3(\text{g})$, $\Delta H_{1300^\circ\text{K}} = -63.1 \pm 2$ kcal.; and CuBr(g) , $\Delta H_{1300^\circ\text{K}} = 23.3 \pm 1.2$ kcal. The D_0 values calculated from the thermal data were 3.80 ± 0.15 and 3.42 ± 0.15 volts for CuCl(g) and CuBr(g) respectively. Free energy equations are given for both cuprous chloride molecular species.

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By Leo Brewer and Norman L. Lofgren
January 2, 1948 -- Contract No. W-7405-eng-48B
For Research, development, or manufacturing work.

University of California,
Radiation Laboratory
Berkeley, California

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Introduction

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⁽¹⁾ noticed the abnormally low entropy of vaporization,

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

unexplained by a dissociation into a monomeric molecule. In addition, from our analysis of vapor density measurements by Wartenberg and Bosse⁽²⁾, Meyer and Meyer⁽³⁾, and Biltz and

(2) Wartenberg and Bosse, Z. Electrochem. 28, 384 (1922).

(3) Meyer and Meyer, Ber. 12, 1112 (1879).

Meyer⁽⁴⁾ who obtained values for the molecular weights of

(4) Biltz and Meyer, Ber. 22, 725 (1889).

cuprous chloride vapors at elevated temperatures, something unusual was suspected. The results of the three molecular weight determinations give values 213 - 216 at 1450°C, 204 at considerably above 1000°C and 187 - 192 at about 1650°C, 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⁽⁵⁾ were unable to arrive at any con-

(5) Maxwell and Mosley, Phys. Rev. 55, 238 (1939).

clusions 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 $(P_{\text{HCl}}/P_{\text{H}_2})^{1/2}$ 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.

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°C 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) A quartz tube 15 mm. outside diameter, and five cm. long containing the cuprous chloride and joined at each end by quartz capillary tubing to minimize diffusion was placed in the furnace mentioned previously. As a carrier gas, argon was used; the volume flow was measured by displacement of water in an inverted 500 cc. burette. 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 passed through the cell and a lense 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 resevoir 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 insure thorough mixing.

Figure 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

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 by Biltz, Fischer, and Juza⁽⁶⁾. An important feature

(6) Biltz, Fischer, and Juza, Z. Anorg. Allg. Chem. 176, 121 (1928).

of the design is that the gaseous mixture may be introduced into the hot evacuated chamber in a reverse direction thus minimizing errors caused by diffusion of cuprous halide vapors into the condensing region before the gas flow is begun. 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 five degrees through use of chromel-alumel thermocouples checked against a calibrated platinum-platinum rhodium couple. In Figure 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

Figure 2.

Volatilization Apparatus.

- A. High pressure cylinder containing hydrogen-hydrogen chloride mixture.
- B. Rotameter
- C. Mercury Manometer
- D. Analysis bulb
- E. High Temperature chamber
- F. Burrell furnace
- G. Absorber
- H. Mercury control manometer with adjustable electrodes, shown enlarged in I.

values arranged to add to 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. (See Figure 2).

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 the reverse 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 $P_{HCl}/P_{H_2}^{1/2}$. 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 reversed 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 condensible 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 condensible 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 was 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 was assumed subject to negligible diffusion error.

The possibility of a thermal diffusion effect causing separation of the hydrogen-hydrogen chloride mixture was also considered, but semi quantitative calculations based on a graphical integration of the differential equation of diffusion flow, ⁽⁷⁾

(7) Unpublished derivation.

$$\frac{dN_1}{dx} = \frac{V_R}{T_R} \times \frac{TN_1}{D} - \frac{WR}{Pa} \times \frac{T}{D} - k_T \frac{1}{T} \frac{dT}{dx}$$

indicated that any separation would be quite small. In the above equation, N_1 = mole fraction of gas (1), W = total gas flow in moles per sec., V_R = gas velocity at room temperature, T_R , D = ordinary diffusion coefficient, which is dependent

upon temperature, and k_t = thermal diffusion coefficient. The calculations show that at a flow rate of four cc. per sec. and with a mole fraction $N_1 = 0.35$ the separation caused an error of approximately 4% in the ratio, PHCl/PH_2 . Since at higher gas velocities the error rapidly decreases, i.e., 0.06% at 40 cc. per sec., the effect was neglected.

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 α , and this must be constant at whatever pressure the gas is withdrawn. Since $N_{\text{HCl}} = 1 - N_{\text{H}_2} = \frac{\alpha}{1+\alpha}$ then the desired ratio in terms of α is

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

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, α . Employing the substitution $\beta = \frac{\alpha^2}{\alpha+1}$, one can find by a simple derivation that the correction for change in β is proportional to the mole fraction of cuprous halide in the gas.

$$\beta = \beta^0 - \left(\frac{\alpha^2}{2} + 2\alpha \right) N_{\text{Cu}}. \quad (3)$$

In equation (3) β^0 represents the quantity $\frac{\alpha^2}{\alpha+1}$ before interaction of the copper and hydrogen chloride, β the same quantity after equilibrium has been attained, and N_{Cu} is the mole fraction of cuprous halide in moles copper/total moles of gas. In Table I are given the results of these calculations for the cuprous chloride system based on experimental values for β^0 , 0.1945 in experiments 24-36 and 0.0290 in 37-43. Table IV for cuprous bromide is based on $\beta^0 = 0.001938$.

TABLE I

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

<u>Exp</u>	<u>Temp</u>	<u>P(total)</u>	<u>P_{CuCl}</u> [*]	<u>P_{HCl}/P_{H₂}</u> ^{1/2}
24	988°K	0.828 atm	1.728x10 ⁻⁴ atm.	0.401
27	988°K	0.824	1.482	0.392
28	988°K	0.824	1.63	0.401
29	988°K	0.828	1.72	0.400
31	1226°K	0.916	4.16	0.420
33	1226°K	0.601	2.35	0.341
32	1226°K	0.266	0.966	0.227
34	1309°K	0.962	6.63	0.432
35	1309°K	0.557	3.815	0.328
36	1309°K	0.203	1.538	0.198
37	1309°K	0.967	1.368	0.163
38	1309°K	0.745	1.18	0.147
39	1309°K	0.452	0.87	0.114
40	1309°K	0.1804	0.509	0.0722
41	1309°K	0.345	0.693	0.0999
43	1268°K	0.859	0.833	0.1584
42	1340°K	0.849	1.740	0.1568

*This column 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.

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, the quantity of hydrogen chloride passed over into the absorber, and the mole ratio, α .

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

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. Hg. allowed analysis of gms. copper per gm. of vapor. After the calculation of chloride by difference, the ratios $\text{Cl/Cu} = 0.97$ and $\text{Cl/Cu} = 1.08$ 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, $P_{\text{HCl}}/P_{\text{H}_2}^{1/2}$.

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

Whereas P_{CuCl} represents the actual partial pressure of cuprous halide in the vapor state, the quantity measureable 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_{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 . In-as-much 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 was 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.

* See Table I

TABLE II

EQUILIBRIUM CONSTANTS FOR REACTION (1).

$T^{\circ}K$	$1/T \times 10^4$	$K_1 \times 10^4$	$3K_3 \times 10^{-4}$	$\log K_1$	$\log 3K_3$
988	10.12	(0.024)**	$25.9 \cdot 10^{-4}$	(-5.63)**	-2.587
1226	8.16	$1.93(^{+}.02)^{*}$	$45.2(^{\pm}0.2)^{*}$	-3.715	-2.345
1268	7.89	4.17	(44)	-3.380	(-2.36)**
1309	7.64	$6.83(^{+}0.16)^{*}$	$43.1(^{+}4.0)^{*}$	-3.166	-2.366
1340	7.46	9.62	(48)**	-3.017	(-2.32)**

Notes--* These values are the result of the mean 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 percent in the case of K_1 and 10 percent in the case of K_3 .

** 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.

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_{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 $(HCl)/(H_2)^{1/2}$ the monomer is a minor 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

$$P_{CuCl}^* - K_1 \left(P_{HCl}/P_{H_2}^{1/2} \right) = P_{Cu_xCl_x}^* = X \cdot K_x \left(P_{HCl}/P_{H_2}^{1/2} \right)^x$$

the log of which gave

$$\log P_{Cu_xCl_x}^* = X \log \left(P_{HCl}/P_{H_2}^{1/2} \right) + \text{constant.} \quad (7)$$

Thus the slope of a plot of $\log P_{Cu_xCl_x}^*$ versus $\log P_{HCl}/P_{H_2}^{1/2}$ would be the polymer number X . In Fig. 3 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⁽²⁾, Meyer and Meyer⁽³⁾, and Biltz and Meyer⁽⁴⁾, the molecular weight was re-evaluated, but by a different procedure. In-as-much as the partial pressure of vapor over liquid

* See Table I

Figure 3.

Polymer Number of Cuprous Chloride Complex
Vapor Molecule.

The data, $\bigcirc$, 1309°K and $\square$, 1226°K, give for the slope
 $X = 3.09$.

cuprous chloride has been quite well established by Maier⁽⁸⁾, Tarasenkov and Kazhy⁽⁹⁾ and Wartenberg and Bosse⁽¹⁰⁾ a measure

(8) Maier, Bureau of Mines T. P. 360(1929).

(9) Tarasenkov and Kazhy, J. Gen. Chem. (U.S.S.R.) 5, 830(1935).

(10) Wartenberg and Bosse, Z. Electrochemie 25, 384 (1922).

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 $\Sigma = -4.575 \log P \text{ atm} + 2.303 \Delta C_p \log T$ versus $1/T$, the following results for the reaction

Cuprous Chloride, (liquid) $\longrightarrow$ Cuprous Chloride(gas).

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

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

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

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

Thus, at the temperature of this experiment, $1119^\circ \pm 5^\circ \text{K}$, a pressure of vapor is calculated to be $0.0668 \text{ atm} (\pm 0.008)$ from equation (8) and the relation $\log P = -\Delta F / 2.303 RT$. 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 experiments to be described subsequently. Table III presents the results of two separate experimental determinations of volatility of liquid cuprous chloride in an argon gas stream which give with the equation, $\text{Mol. Wt.} = (\text{GmCuCl}) RT/PV$,

TABLE III

VOLATILITY OF CUPROUS CHLORIDE IN AN ARGON GAS STREAM.

	<u>Expt. 1.</u>	<u>Expt. 2.</u>
T	1119 $\pm$ 5°K	1119 $\pm$ 10°K
mg CuCl	212.0	171.0
V(A over H ₂ O)	265.0 cc.	189.7 cc.
T(A over H ₂ O)	297.2°K	299.6°K
V(1119°K)	968 cc.	687 cc.

values of 300 ± 36 and 341 ± 55 respectively. Inasmuch as the actual error limits are probably less than the quantities specified, these results are taken to be a confirmation of previous conclusions, namely that the molecular species is of a trimeric form, Cu_3Cl_3 .

Likewise a value for 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 $1141 \pm 5^\circ\text{K}$. 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 ± 34 .

Heat of Formation of $\text{CuCl}(\text{g})$. -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 Σ function, tabulated in Table IV, ΔH_0 was gotten as the slope of the Σ versus $1/T$ plot shown in Fig. 4. The $\Delta C_p = -1.81$ was inserted in order to improve the extrapolation properties of the equation, and was calculated assuming $C_p(\text{CuCl}) = 8.80$, $C_p(1/2 \text{H}_2) = 3.73$, $C_p(\text{HCl}) = 7.84$ and $C_p(\text{Cu}) = 6.50$.

TABLE IV

Σ Function for Reaction: $\text{Cu(s)} + \text{HCl} = \text{CuCl(g)} + 1/2 \text{H}_2$.

<u>T°K</u>	<u>1/T</u>	<u>-4.575 log K</u>	<u>-4.17 log T</u>	<u>Σ</u>
1226	$8.16 \cdot 10^{-4}$	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

From Fig. 4, with the uncertainties indicated by means of the circle radii, ΔH_0 is found to be 49.32 ± 4 kcal. which gives the following equations of free energy, heat, and entropy of reaction:

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

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

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

Through use of the entropy of reaction (11) given by Equation (14) and the entropies of copper, hydrogen chloride, and hydrogen at 1300°K as given by Brewer^(11, 12) ($S_{\text{Cu}} = 17.28$, $S_{\text{HCl}} = 55.29$, and $S_{\text{H}_2} = 41.68$ e.u.) the entropy of the gaseous molecule, CuCl, was calculated to be 73.8 ± 4 e.u. at 1300°K.

(11) Brewer "The Thermodynamic Properties of Common Gases"

Atomic Energy Commission Declassified Report.

(12) Brewer "The Thermodynamic and Physical Properties of the Elements", Declassified Atomic Energy Commission

Paper.

An alternate calculation of the entropy of the diatomic molecule, using Spectroscopic data by Ritschl⁽¹³⁾ who gives $W_0 = 415.3 \text{ cm}^{-1}$ and also using an estimate of interatomic distance by Stevenson⁽¹⁴⁾ who gives $d = (2.00 \pm 0.05) 10^{-8} \text{ cm}$, produces a value

(13) Ritschl, Z. Phys. 42, 172 (1927).

(14) Stevenson, J. Chem. Phys. 8, 898 (1940).

Figure 4.

Plot for Reaction:

of 69.6 ± 0.5 e.u. The uncertainty indicated in the final result arises from the application of a $0.15 \cdot 10^{-8}$ cm uncertainty to the interatomic distance to allow for a possible variation of d . Kelley⁽¹⁵⁾ gives the equations required for the calculation.

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

It is thus apparent that the indicated slope of the function plot in Fig. 4 may be in error by approximately 6 kcals. 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. Revision of the thermodynamic equations, to give the observed free energy of reaction and the calculated entropy, results in the following equations:

$$\Delta F = 43,660 - 14.17 T \log T - 31,80 T \quad (12')$$

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

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

Heat of Formation of $\text{Cu}_3\text{Cl}_3(\text{g})$. -Because of the uncertainty of the ΔG_p for the reaction and the apparent inaccuracies in the data ΔH was evaluated as the slope of the $\log K$ versus $1/T$ function. Thus for the reaction,

in the neighborhood of 1300°K , we find the results,

$$\Delta F = 4,500 + 9.4 T \quad (16)$$

$$\Delta H = 4,500 \pm 2,000 \text{ (Cal)}$$

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

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) $\Delta H = 4.5 \pm 2 \text{ kcal.}$ and the heat of formation of hydrogen chloride at 1300°K , -22.53 kcal. , from Brewer⁽¹¹⁾, the heat of reaction(17),

is found to be $-63.1 \pm 2 \text{ kcal.}$ The heat of formation of cuprous chloride liquid, $\Delta H_{1300^\circ\text{K}} = -26.6 \pm 3 \text{ kcal}$, has been evaluated by Brewer, Bromley, Gilles, and Lofgren⁽¹⁶⁾ from the heat of

(16) Brewer, Bromley, Gilles, and Lofgren, "The Thermodynamic Properties of the Halides". Declassified Atomic Energy Commission Paper, CC-3585, October 15, 1945.

formation of solid cuprous chloride, $\Delta H_{298} = -32.6 \pm 0.4$ kcal., and estimated heat capacities 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 to 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 $-63.1(\pm 2)$ kcals. from experiment.

Cuprous Bromide Equilibrium Constants. - In Table V 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 $P_{\text{CuBr}}^* - P_{\text{HBr}}/P_{\text{H}_2}^{1/2}$ relations of this system and that of the cuprous chloride system. The equilibrium constants have been tabulated in Table VI, in which they are arrived at first assuming monomer and trimer and secondly assuming monomer and dimer. This is done merely to allow for the possible existence of the dimer inasmuch as cuprous bromide vapor pressures obtained by Jellinek and Rudat⁽¹⁷⁾ using a dynamic method similar to that employed in this paper, indicate the approximate dimer

(17) Jellinek and Rudat, Z. Physikal Chem. A 143, 55 (1929).

composition in the vapor. The vapor pressure data of Wartenberg and Bosse⁽¹⁸⁾ was required for this calculation. However, it is quite possible that under the conditions of these experiments

* See Table V.

TABLE V

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

<u>Exp.</u>	<u>T</u>	<u>P(total)</u>	<u>P_{CuBr}[*]</u>	<u>P_{HBr}/P_{H₂}^{1/2}</u>
45	1323°K	0.2956(atm)	1.900 · 10 ⁻⁴ (atm)	0.02355
47	1323°K	0.5165	2.635	0.03125
48	1323°K	0.7623	3.507	0.0380
49	1323°K	0.964	4.24	0.0428
50	1351°K	0.1998	1.724	0.01930

* See Table I.

(18) Wartenberg and Bosse, Z. Electrochem. 28, 384 (1922).

the vapor consists of a mixture of monomer and trimer and that the existence of a composition indicating dimer is merely coincidental. This possibility is qualitatively upheld both by the data of Jellinek and Rudat which actually indicates a molecular weight about thirty units above the dimeric molecular weight at 1250°K and by the hydrogen - hydrogen bromide equilibrium data which exhibits a considerably lesser polymer stability than does the corresponding cuprous chloride data. Therefore, in view of this uncertainty both constants are included in Table VI.

TABLE VI

Equilibrium Constants for Reaction $\text{XCu(s)} + \text{XBr} = \text{Cu}_x\text{Br}_x + x/2 \text{H}_2$.

<u>T</u>	<u>1/T</u>	<u>K₁</u>	<u>3K₃</u>	<u>K₁</u>	<u>2K₂</u>
1323°K	$7.56 \cdot 10^{-4}$	$7.17(\pm 0.19) \cdot 10^{-3}$ *	$1.45(\pm 0.16)$ *	$5.36(\pm 0.59) \cdot 10^{-3}$ *	$0.104(\pm 0.016)$ *
1351°K	$7.40 \cdot 10^{-4}$	8.4	(1.45)**		

* See Table I

** See Table II

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),

$$\Delta F = -126.4 - 12.51 T \log T + 104.7 T. \quad (19)$$

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 VII. It is quite apparent that at a temperature in the neighborhood of 1750°K, the region investigated by Wartenberg and Bosse⁽²⁾, Meyer and Meyer⁽³⁾, and Biltz and Meyer⁽⁴⁾ 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.

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

TABLE VII

DISSOCIATION OF GASEOUS CUPROUS CHLORIDE POLYMER AT HIGH

TEMPERATURES: $\text{Cu}_3\text{Cl}_3(\text{g}) = 3 \text{ CuCl}(\text{g})$.

<u>T</u>	<u>P</u>	<u>K</u>	<u>%CuCl</u>	<u>%Cu₃Cl₃</u>
1000°K	0.0218 *atm.	$1.15 \cdot 10^{-13}$	.0014	100.0 -
1632°(b.p.)	1.00 *	$1.495 \cdot 10^{-3}$	11.0	89.0
1750°	1.00	$1.79 \cdot 10^{-2}$	23.9	76.1
2000°	1.00	1.11	69.6	30.4

* Saturated Vapor

of cuprous and silver halides, both were included in the summary calculations shown in Table VIII. 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.

TABLE VIII⁽¹⁹⁾

VAPORIZATION OF CUEROUS AND SILVER HALIDES
TO MONOMERIC GAS AT 1300°K. $MX(l) = MX(g)$.

<u>MX</u>	<u>$\Delta F_{1300^\circ K}$</u>	<u>$\Delta H_{1300^\circ K}$</u>	<u>$\Delta S_{1300^\circ K}$</u>
CuCl	15.8(± 3) kcal	46.5(± 3)*kcal	23.6(± 5) e.u.
CuBr	13.5(± 3)	45.1(± 4)	24.3(± 5)
CuI	> 3.9	> 39.0	27.0(± 5)
AgCl	12.9(± 2)	43.4(± 3)	23.5(± 1)
AgBr	10.5(± 1)	40.3(± 3)	23.3(± 2)
AgI	9.8(± 1)	39.8(± 3)	23.1(± 2)

* Calculated from ΔF and ΔS of vaporization at 1300°K instead of from equation (13).

(19) References to Table VIII.

Free Energies of Vaporization. - For CuCl and CuBr the equilibrium data of Equation (12) and Table VI were employed to obtain the ΔF of formation of the gaseous molecules and the Halide Report, by Brewer et al.⁽¹⁶⁾ to obtain the ΔF of formation of the liquid at 1300°K. For CuI (see section on iodide polymer) vapor pressures by Jellinek and Rudal⁽¹⁷⁾ and Wartenberg and Bosse⁽¹⁸⁾ give an uncertain value for ΔF_v . For AgCl, AgBr and AgI, Maier⁽⁸⁾ Von Wartenberg and Bosse⁽²⁾, Jellinek and

Rudat⁽¹⁷⁾ give vapor pressures which are presented by Kelley⁽¹⁾.

Entropies of Vaporization. - Entropies of the gaseous molecules were calculated by means of the Sachur-Tetrode Eqn., through use of spectroscopic data tabulated by Herzberg⁽²¹⁾ and

(21) Herzberg, "Diatomic Molecules". Prentice Hall, (1939).

Stevenson's⁽¹⁴⁾ interatomic distances. Entropies of the liquids at 1300°K were procured from the Halide Report by Brewer⁽¹⁶⁾ from which the ΔS_v was acquired by difference.

Heats of Vaporization. -The relation, $\Delta H = \Delta F + T\Delta S$ was employed.

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⁽²¹⁾ and Gaydon⁽²²⁾ and are included as column three

(22) Gaydon, "Dissociation Energies". Chapman and Hall Ltd. (1947).

of Table IX with the number of vibrational states measured. At the same time, by means of the ΔF of formation of the gaseous

molecules from 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 ΔH_0 was possible. In this calculation, $\Delta F - \Delta H_0$ values from Brewer^(11, 12) and Brewer, Bromley, Gilles, and Lofgren⁽¹⁶⁾ were required. These thermo-chemical calculations (T.C.) are summarized in column two of Table IX.

TABLE IX
DISSOCIATION ENERGIES.

<u>MX</u>	<u>D₀(T.C.)</u>	<u>D₀(L.B.X.)</u>
CuCl	3.80 ($\pm$ 0.15)	3.3 (0-11)
CuBr	3.42 ($\pm$ 0.15)	3.5 (0-9)
CuI	< 3.25	3.0 (0-15)
AgCl	3.28 ($\pm$ 0.1)	3.11 (0-9)
AgBr	3.02 ($\pm$ 0.1)	2.77 (0-15)
AgI	2.67 ($\pm$ 0.1)	3.0 (0-17)*

* Probably in error because of ionic forces.

Polymer in the Cuprous Iodide System. -At the temperature of the vapor pressure determinations by Von Wartenberg and Bosse⁽¹⁸⁾ 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 VIII and IX, 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⁽¹⁷⁾ in which the weight of halide in the vapor was determined. Application of the data of Von Wartenberg and Bosse⁽¹⁸⁾ after subtraction of the iodine partial pressure indicates a vapor of average molecular weight, 116, compared with a theoretical value of 99 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 Mol. wt.

Structure of the Trimer Molecule. -The electron diffraction results by Maxwell and Moseley⁽⁵⁾ 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 stability of the trimer its structure may be cyclic, as is benzene, with alternate copper and halogen atoms. This form of the molecule also would have electron diffraction properties such as were actually found.

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