[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Structure of Mercurous Chloride Vapor

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The nature of calomel vapor has been investigated recently by Gucker and Munch[1] who show that, in the neighborhood of 400°, vapor density measurements are consistent with the formula HgCl, or with the mixture, Hg + $HgCl_2$. The formula Hg_2Cl_2 is excluded by their observations. They also obtained spectroscopic evidence of the presence of free mercury at all temperatures above 250°, in even the most carefully dried calomel.

The formula HgCl implies an odd number of electrons. Magnetic susceptibility measurements were therefore undertaken in an effort to decide whether calomel vapor should be considered as HgCl or as a mixture of mercury and mercuric chloride.

Magnetic measurements on the solid,[2] and on the liquid,[3] have already shown mercurous chloride to be diamagnetic.

Experimental Part

The magnetic measurements were carried out on a Gouy balance after considerable time had been spent in an unsuccessful attempt to devise a more sensitive torsion method. The calomel used was thoroughly washed with water, air dried, and then sealed into a series of glass bulbs connected to a high-vacuum system. The sample tube was sealed on to the system. This tube was of the familiar double-ended type, constructed of Pyrex glass 5.8 mm. in internal diameter. The calomel was contained in the lower part of the tube as it hung in the balance. A liquid-air trap was inserted before the diffusion pump in the vacuum system.

The calomel was then sublimed from part to part of the system, the free parts of the apparatus being thoroughly torched, in order to dry the calomel according to the directions of Gucker and Munch. About half a gram of calomel was finally sublimed into the sample tube which was then sealed off while the whole apparatus remained under the highest obtainable vacuum.

The tube was then transferred to the Gouy balance. Temperature control was obtained by means of a long thin electric furnace designed to fit between the pole-pieces of the magnet. The pole-pieces were cooled with water running through lead tubing. An inert atmosphere was maintained in the furnace by allowing nitrogen to enter it at the rate of a few cubic centimeters per hour. Measurements on the empty tube had previously established the reproducibility of weighings at about ±0.01 mg. except at room temperature where the reproducibility was ±0.001 mg. The principal source of error was in erratic weighings, probably due to slight convection currents set up in the furnace at the higher temperatures. The field strength for all measurements was 13,300 oersteds. The apparatus was calibrated by filling the tube with oxygen at room temperature and pressure.

Actual measurement of temperature in the Gouy method is often uncertain, because of the impossibility of placing a temperature measuring device in the sample being weighed. In the present work this difficulty was overcome by letting the sample be its own thermometer by virtue of the buoyancy of the nitrogen atmosphere acting on the sample tube. A simple calculation, involving the volume of the tube and the density of the atmosphere, related the temperature to the difference in apparent weights of the sample tube at room temperature and at any other temperature. This method proved so successful that it might well be used in place of more cumbersome methods for all Gouy susceptibility measurements.

A little difficulty was experienced when the calomel sublimed to cover the whole inner surface of the sample tube. This gave results which might have been interpreted as strong diamagnetism of the vapor, but which were actually due to the solid. This difficulty was overcome by having one end of the sample tube a degree or two cooler than the other. The calomel then promptly sublimed to the cooler end and remained there while the weighings were being made.

Results

The results obtained are most readily presented by comparing the observed change in weight (on application of the field) with the change to be expected if the formula for mercurous chloride is HgCl. The apparatus was not sufficiently sensitive to detect the diamagnetism of gases. The diamagnetic correction is therefore omitted in this calculation.

The force, in dynes, exerted on a Gouy sample tube is given by $f = {}^1/_2 \mathrm{K}H^2A$, where K is the susceptibility per unit volume, H is the field strength, and A the cross-sectional area of the sample tube. Hence the change in weight on application of the field is

$$\Delta w = \frac{\mathrm{K}H^2A}{2g}$$

The molar susceptibility of a paramagnetic vapor possessing single unpaired electron spin is about 1180×10^{-6} at 0°, or at any other temperature $1180 \times 10^{-6} \times (273/T)$. The gram susceptibility is then

(1) Gucker and Munch, THIS JOURNAL, 59, 1275 (1937). These authors summarize the literature up to date.

(2) "International Critical Tables," Vol. 6, p. 357.

(3) Farquarson and Heymann, *Trans. Faraday Soc.*, 31, 1004 (1935).

$$\chi = \frac{1180 \times 10^{-6} \times 273}{MT}$$

where M = the molecular weight.

The volume susceptibility is

$$\kappa = \frac{1180 \times 10^{-6} \times 273\, d}{MT}$$

where d is the density.

The density at temperature T and pressure p is approximated by

$$d = \frac{273\, Mp}{22{,}400T \times 760}$$

Substituting for d

$$\kappa = \frac{1180 \times 10^{-6} \times (273)^2\, p}{22{,}400T^2 \times 760} = 5.16 \times 10^{-6}\, p/T^2$$

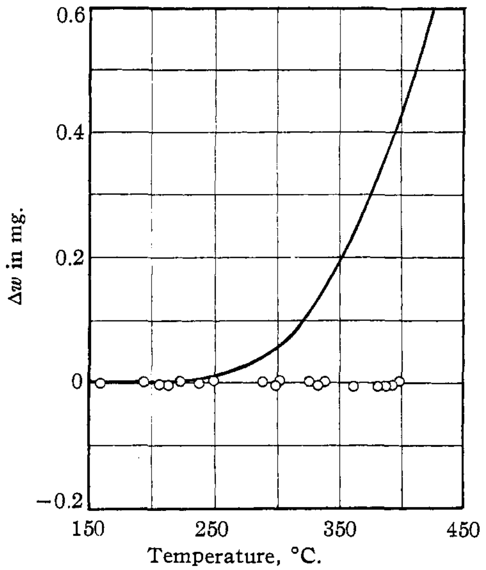

Fig. 1.—The upper curve shows the theoretical Δw expected for the formula HgCl. The experimental points show the observed Δw's.

That is, for a paramagnetic vapor in equilibrium with its solid or liquid, the susceptibility varies directly as the vapor pressure and inversely as the square of the absolute temperature.

In the present case

$$\Delta w = 0.236p/T^2$$

The vapor pressures of calomel were obtained from the "International Critical Tables."[4] The theoretical Δw ranges from 0.5 microgram at 180° to 313 micrograms at 370°. If the compound HgCl had been found to exist, its paramagnetism should have become measurable at about 250°.

These theoretical results, together with the observed results, are given in Fig. 1.

It will be seen that there is no indication whatever that HgCl exists. The evidence appears to be conclusive between the temperatures 250 and 375°.

In conjunction with the work of Gucker and Munch, these results show that the structure of mercurous chloride vapor is neither Hg_2Cl_2 nor HgCl, but is a mixture of Hg and $HgCl_2$ between the temperatures 250 and 375°, and probably at higher temperatures also. The alternative formulas are not excluded for the vapor below 250°. Except, however, for that region, the monomeric formula, HgCl, is definitely ruled out for the structure of the solid, liquid and vapor.

Summary

Measurements of magnetic susceptibility on mercurous chloride vapor between the temperatures 250 and 375° show it to be diamagnetic. This work excludes the monomeric formula, HgCl.

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(4) "International Critical Tables," Vol. III, pp. 208 and 214.