The non-volatile portion of the reaction mixture, when worked up, yielded a small amount of ethyl acetate but mainly a non-distillable condensation product.

With magnesium the iodo ester reacted without a solvent at room temperature. Removal of the volatile portion of the reaction mixture gave a considerable amount (43%) of ethyl iodide. The non-volatile portion of the reaction mixture in this case also was found to consist mainly of non-distillable material.

In ether solution ethyl orthoiodoacetate reacted with magnesium at temperatures as low as 5°, but even at this low temperature polyintermolecular condensation could not be avoided. While no ethyl iodide was produced, the main reaction product appeared to be the same type of non-distillable material which had been obtained in the other runs. In addition to this indefinite product small amounts of ethyl acetate and diethyl succinate were isolated by distillation.

The authors wish to express their gratitude to the Wisconsin Alumni Research Foundation for a grant that made this work possible.

Summary

Procedures for the preparation of ethyl orthochloro-, -bromo-, and -iodoacetates are described. Of these orthohalogeno esters the chloro compound is too inert to react with either zinc or magnesium. Both the bromo and iodo esters react with these metals to form organo-metallic halides which then undergo poly-intermolecular condensation to give indefinite, non-volatile products. There was no evidence that these organo-metallic halides decomposed intramolecularly into ketene acetal and an ethoxymetallic halide.

MADISON, WISCONSIN RECEIVED APRIL 30, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Nature of Calomel Vapor[1]

BY FRANK T. GUCKER, JR., AND RALPH H. MUNCH

Introduction

Calomel vapor has been studied by numerous investigators for more than a century, yet its exact composition is still in doubt. A good critical discussion of the earlier work is contained in an article by Alexander Smith and Menzies.[2] In 1833, E. Mitscherlich[3] determined its vapor density and found that it corresponded to the formula HgCl. This conclusion was confirmed by the later work of Deville and Troost,[4] Rieth,[5] and Harris and Victor Meyer.[6] All of these results were obtained at temperatures from 450° to somewhat above 500°. In 1864, W. Odling[7] discovered that a piece of gold leaf exposed to calomel vapor became amalgamated. He concluded that calomel vapor is decomposed to some extent at least, presumably into mercuric chloride and mercury, and this conclusion was confirmed by others. In 1894, W. Harris and Victor Meyer[6] attempted to find the extent of the dissociation by separating the mercury and mercuric chloride vapors by diffusion through a porous clay tube. Since they obtained a large amount of free mercury in this way, they argued that the dissociation is nearly complete. This conclusion, however, is not justified, since the removal of the mercury would cause increased dissociation, even if the original dissociation had been slight. No method which changes the concentration of any constituent in the equilibrium will give a reliable estimate of its extent.

Smith and Menzies,[2] realizing that no qualitative experiments could solve the problem, devised a quantitative method based on a study of the vapor pressures of mercury, calomel, and a mixture of the two, at temperatures from 360 to 400°. If calomel and mercury are immiscible and their vapors neither react nor have a common component, the vapor pressure of the mixture would be the sum of the vapor pressures of the constituents. On the other hand, if calomel and mercury are immiscible and the calomel vapor is completely dissociated into mercuric chloride and mercury, the vapor pressure of the mixture would be less than the sum of the vapor pressures of the constituents. They found experimentally that calomel is slightly soluble in mercury, and that the vapor pressure of the mixture corresponds to that calculated for the case of complete dis-

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(1) Parts of this paper were presented at the Midwest Sectional meeting of the American Chemical Society at Louisville, November, 1935.

(2) Smith and Menzies, THIS JOURNAL, **32**, 1541 (1910).

(3) E. Mitscherlich, *Pogg. Ann.*, **29**, 193 (1833).

(4) Deville and Troost, *Compt. rend.*, **45**, 821 (1857).

(5) R. Rieth, *Ber.*, **3**, 666 (1870).

(6) W. Harris and Victor Meyer, *ibid.*, **27**, 1482 (1894).

(7) W. Odling, in private communication cited by Williamson, *J. Chem. Soc.*, **17**, 211 (1864).

sociation, with the vapor pressure of the mercury decreased by the calomel dissolved in it. At 400°, then, their work indicated that calomel is completely dissociated according to the equation

$$2HgCl = Hg + HgCl_2$$

Since the mean molecular weight of the dissociated products still corresponds to the formula HgCl, this work was consistent with that which had gone before, except for the work of H. B. Baker,[8] who reported that, when the calomel was carefully dried with phosphorus pentoxide for three weeks in the dark, its vapor density at 445° corresponded to the double formula Hg_2Cl_2.

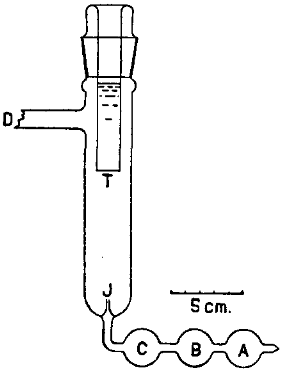

Fig. 1.—Sublimation apparatus.

The recent discussion of the heats of formation of the gaseous halides of mercury by H. Sponer[9] corroborates the idea of the dissociation of calomel vapor. K. Wieland has studied the emission spectrum[10a] in a discharge through mercuric chloride vapor and also the fluorescent spectrum[10b] of this vapor. Parts of these spectra arise from mercurous chloride molecules. From a partial analysis of the emission spectrum, Sponer calculated that the energy of dissociation of mercurous chloride into normal mercury and chlorine atoms is approximately 1.4 electron volts or 32 kcal. Combining this value with the known heats of formation of mercuric chloride and other necessary thermal data, she calculated that the dissociation of gaseous mercurous chloride *liberates* 40 kcal.[11]

$$2HgCl(g) \longrightarrow HgCl_2(g) + Hg(g) + 40 \text{ kcal.}$$

The same reaction for the solid halides *absorbs* heat

$$2HgCl(s) \longrightarrow HgCl_2(s) + Hg(l) - 11 \text{ kcal.}$$

These values are consistent with the chemical evidence for the stability of solid calomel and its dissociation in the gas phase. Sponer also found that the heat of vaporization of calomel is abnormally large.

$$HgCl(s) \longrightarrow HgCl(g) - 43 \text{ kcal.}$$

This is twice as great as that of mercuric chloride. She concluded that this energy stabilizes the mercurous chloride in the solid state.

With these results in mind, we were interested to see what new facts we could learn about calomel vapor and what light these might throw upon its constitution. Is the decomposition of calomel vapor complete at all temperatures at which vaporization is appreciable, or is it incomplete below the temperature of 360° where Smith and Menzies worked?

Sublimation Experiments.—Preliminary experiments, designed to detect decomposition occurring at low temperatures, were made by shooting a jet of calomel vapor at a target cooled with liquid air to freeze the equilibrium of the gas phase. The apparatus is shown in Fig. 1. Calomel was placed in the bulb A. The entire apparatus was then evacuated through D by means of a mercury diffusion pump and liquid-air trap. Approximately three-quarters of the calomel was now sublimed out of A at about 250°. The first quarter was discarded through the jet, J, and the outlet tube. The middle portion was collected in B, whence it was fractionated as before into C. The target, T, was now cooled by filling the reëntrant tube with liquid air. The purified calomel was vaporized at about 200°, forming a jet of vapor which struck the target, T, and condensed upon it. At the end of the experiment, the apparatus was opened to the air and the target was removed and examined under a low-power microscope. There was no indication of the presence of mercury, indicating either that no decomposition had occurred in the beam or that recombination had taken place on the target. To test the second alternative, a mixture of C. P. mercury and C. P. mercuric chloride was placed in C. The system was evacuated and after the pumps had run for some time, the mixture was sublimed through the jet. The deposit on the target contained mercury, even though more than enough mercuric chloride was present to react with all the mercury. These experiments indicated that carefully dried calomel vapor does not decompose at 200°.

Ultraviolet Absorption Experiments.—To obtain more direct and independent evidence we decided to utilize the absorption of the mercury resonance line at 2537 Å. as an indication of mercury in the vapor. The usefulness of this method of detecting mercury is well illustrated by W. G. and P. A. Leighton[12] in an article which appeared while this work was in progress.

The necessary intense source of ultraviolet light which we used was a new low-voltage hydrogen arc developed for this work and already described.[13] After passing through a quartz lens of 15-cm. focal length and an absorption cell, the light from the arc was focused upon the slit of a small Littrow-type quartz spectrograph manufac-

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[8] H. B. Baker, *J. Chem. Soc.*, **77**, 646 (1900).

[9] H. Sponer, *Z. physik. Chem.*, **B11**, 425 (1931).

[10] K. Wieland, (a) *Helv. Phys. Acta*, **11**, 46 and 77 (1929); (b) *Z. Physik*, **77**, 157 (1932).

[11] The value of 28 kcal. for the same reaction may be obtained from the article of H. Ootuka and G. Schay [*Z. physik. Chem.*, **1B**, 68 (1928)] who combined thermochemical data with the results of A. Terenin [*Z. Physik*, **44**, 713 (1927)] for the continuous absorption of mercuric chloride vapor and the resulting fluorescent bands. The value of 28 kcal. is in qualitative agreement with that of Sponer, although the method is less reliable.

[12] W. G. Leighton and P. A. Leighton, *J. Chem. Ed.*, **12**, 139 (1935).

[13] R. H. Munch, THIS JOURNAL, **57**, 1863 (1935).

tured by Bausch and Lomb. The absorption cells were made by sealing a disk of optically-finished fused quartz to each end of a quartz tube 2.5 cm. in diameter. One of the cells was 2.5 and the other 25 cm. long. Each was provided with a side-arm of quartz tubing through which material was introduced.

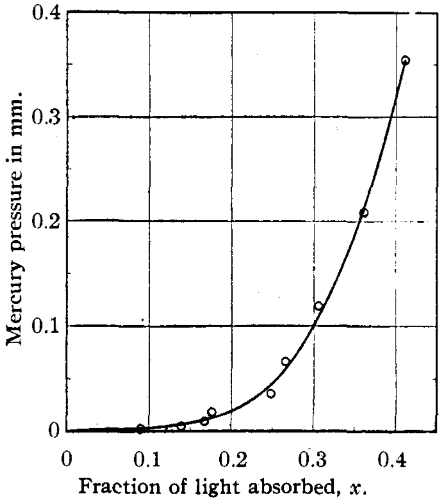

Fig. 2.—Absorption curve.

The absorption method is extremely sensitive. The photographs clearly indicate the presence of mercury in the 25-cm. tube at 23°, where the vapor pressure is only 0.0015 mm.

In our first series of experiments, C. P. calomel, which was not especially dried or purified, was introduced into the cell. The side-arm was left open to the atmosphere. This vapor showed detectable quantities of mercury at temperatures from 450° down to 100°. Numerous blank experiments showed that this absorption was not due to mercury vapor in the air of the room or in the spectrograph.

An attempt to determine the amount of mercury vapor present in the calomel was first made by a visual comparison of plates showing the absorption of the 2537 Å. line by calomel vapor and by mercury vapor at known temperatures, read to 0.25° by a copper-constantan thermel and potentiometer. The vapor pressure of the mercury at different temperatures was taken from the tabulation in the "International Critical Tables."[14] This visual method showed that the pressure of mercury in the undried calomel vapor corresponds to about half the total calomel vapor pressure—in other words, that decomposition is complete over this range.

The method was improved by the application of the technique of photographic photometry.[15] By making a series of equally-timed exposures, with a suitable set of rotating sector disks, and taking a microphotometric trace of the plate, we could plot a *blackening curve* showing the light intensity corresponding to any galvanometer deflection.

From a series of measurements with the cell filled with mercury vapor at known temperatures (and hence known vapor pressures) a curve was drawn showing the mercury pressure as a function of the fraction of light absorbed, x. On this curve, which is reproduced in Fig. 2. the average deviation of the points is 0.005 mm. and the maximum is 0.01 mm. From it we could read the mercury pressure in calomel vapor at any temperature at which we had measured the absorption. The results for undried C. P. calomel over a temperature range of 120 to 180° are given in Table I. We have also included for comparison the vapor pressure of calomel at the same temperatures, taken from a linear plot of the logarithm of the vapor pressure against the reciprocal of the absolute temperature, shown in the upper half of Fig. 3. The data are those of Smith and Menzies[2] and Smith and Calvert[16] at high temperatures (310–403°) and of Stelzner and Niederschulte[17] at 10° intervals from 180 to 90°. The former were determined by a static method; the latter by weighing the amount of calomel evaporating into a stream of air under known conditions. This method, of course, assumes a normal molecular weight for the compound. As Fig. 3 shows, the high-temperature results agree well with those at lower temperatures, except for a systematic deviation at the temperatures 120–90°, which is not surprising in view of the low vapor pressure in this region. The results from 130 to 90° are listed as "less accurate" in the "International Critical Tables."[18]

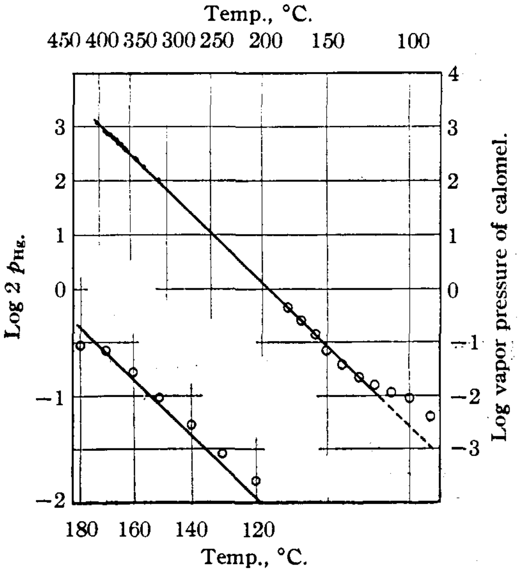

Fig. 3.—Vapor pressure of calomel and partial pressure of mercury: upper line, vapor pressure of calomel; ●, Smith *et al.*; ○, Stelzner and Niederschulte; lower line, vapor pressure of calomel—circles represent twice the partial pressure of mercury.

The data of Table I show that the partial pressure of the mercury in undried calomel vapor is about half of the vapor pressure of the calomel, from 120 to 180°. This result is

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[14] "I. C. T.," Vol. III, p. 206.

[15] For a discussion of the theory of this method, see K. B. Thomson and O. S. Duffendack, *J. Opt. Soc. Am.*, **23**, 101 (1933).

[16] Smith and Calvert, THIS JOURNAL, **38**, 801 (1916).

[17] Stelzner and Niederschulte, *Ber. deut. physik. Ges.*, **3** 159 (1905). Quoted by Maier, Bur. of Mines Tech. Paper No. 360, p. 25.

[18] "I. C. T.," Vol. III, p. 208.

TABLE I

PARTIAL PRESSURE OF MERCURY IN CALOMEL VAPOR COMPARED WITH THE VAPOR PRESSURE OF CALOMEL

The column headings are: Temp. in °C.; x the fraction of light absorbed at 2537 Å.; p_{Hg} the partial pressure of mercury in the calomel vapor calculated from the absorption; p_{HgCl} the vapor pressure of calomel read from the graph of Fig. 3; $\Delta p = p_{Hg} - {}^1/_2\, p_{HgCl}$ and $\%\Delta = 100\,\Delta p/0.5\, p_{HgCl}$.

Temp.	x	p_{Hg}	p_{HgCl}	$\frac{p_{Hg}}{p_{HgCl}}$	Δp	$\%\Delta$
120	0.146	0.007	0.011	0.64	+0.0015	30
130	.177	.013	.022	.59	+ .002	18
140	.220	.027	.045	.60	+ .0045	20
150	.245	.048	.083	.58	+ .0065	16
160	.288	.083	.15	.55	+ .008	11
170	.311	.119	.25	.48	− .006	5
180	.330	.148	.45	.33	− .076	34
			Av.	.55	Av.	19

TABLE II

THE MOLECULAR WEIGHT OF CALOMEL VAPOR AT 375–430°

Temp., °C.	Pressure, mm.	Vol., ml.	Calomel, g.	Mol. wt.
423	573	319.2	0.9889	234.7
404	559			234.0
393	553			232.8
375	539			232.3
430	599	319.2	1.0431	239.2
416	585			240.2
375	571			240.6
			Average	236.3
Molecular weight for formula HgCl is				236.07

shown graphically in the lower half of Fig. 3, where the line corresponds to the vapor pressure of calomel taken from the upper half of the figure, and the circles correspond to twice the partial pressure of mercury observed in the calomel vapor. The deviations correspond to an average of ±0.005 mm. in the determination of the partial pressure of mercury, excepting the result at 180° which deviates by 0.078 mm. Although the fraction of light absorbed in this case is so large that the mercury pressure must be read from the steep part of the curve in Fig. 2, where the sensitivity is low, this error is considerably greater than we would expect. The average *percentage* deviation is 19 and the maximum is 34%.

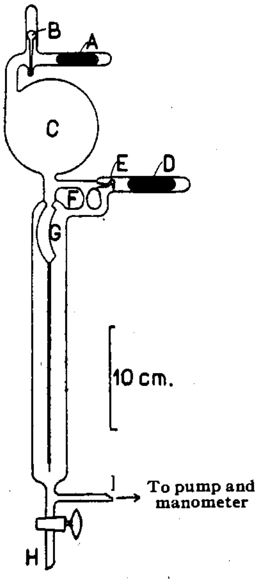

Fig. 4.—Vapor density apparatus.

We next investigated the absorption of the 2537 Å. line in carefully dried calomel vapor. C. P. calomel was placed in the absorption cell, the side-arm of which was sealed by means of de Khotinsky cement to a vacuum system consisting of a liquid-air trap and mercury diffusion pump backed by a Cenco Hyvac. After establishing the best possible vacuum, the calomel was sublimed from one end of the cell to the other, while the parts of the cell which did not contain calomel were successively heated nearly to redness, until the whole cell had been baked. After about three hours of this treatment, the quartz side-arm of the cell was sealed off, leaving the calomel *in vacuo*.

When the vapor of this dried calomel was examined spectroscopically at various temperatures up to 200°, no trace of absorption at 2537 Å. was observed, even when the absorption tube was held at this temperature for twenty hours. Attempts to study the vapor at higher temperatures were temporarily balked because, when the vapor pressure of calomel exceeded 0.6 mm., it became opaque a little below 3000 Å. This absorption, which did not appear in the vapor of undried C. P. calomel, is general and does not show a structure corresponding to the emission bands of HgCl which Wieland[10,19] observed from 2400 to 2650 Å. The difficulty with the general opacity was overcome by keeping the pressure of the calomel vapor at about 0.6 mm. The side-arm, through which the cell had been filled, was maintained at a temperature of 200° while the rest of the tube was heated to the desired temperature. In this way the behavior of the vapor at higher temperatures was investigated. The cell was heated to 400° and exposures were made at 50°-intervals down to 150°. The spectra showed the absorption due to mercury vapor down to 250°, although we did not measure the amount of mercury quantitatively. Below 250° the mercury absorption line disappeared. This behavior is strikingly different from that of the original C. P. calomel. It did not result from any permanent alteration, for when the tube was opened to the air of the laboratory, the vapor again showed the mercury absorption line at low temperatures. We did not study the point any further and can offer no explanation of this peculiar effect. It may be due to the scrupulous drying which, according to Baker,[8] prevents the vapor from amalgamating with gold foil. However, it is hard to see how this factor could shift the dissociation equilibrium, which is supposed to give rise to the mercury vapor. Possibly the removal of the gases of the atmosphere may cause the change. We hope to investigate this point more fully in this Laboratory in the near future. Whatever the cause of the phenomenon, these results agree with our earlier sublimation experiments, which were carried out with dried calomel, *in vacuo*.

Vapor Density Measurements.—Because of the striking effect of careful purification upon the decomposition of calomel vapor, a measurement of the vapor density of this material seemed interesting. For this purpose we used the all-glass apparatus shown in Fig. 4. It consisted of a bulb, C, into which a weighed amount of calomel could be introduced from a sealed capsule, B. The temperature of the vapor was known and its pressure was measured via the null-point gage, G. This gage was made according to the method of Jackson[20] by blowing a long thin-walled bulb and then heating one side until it drew in parallel to the

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(19) Sponer, "Molekülspektren," Verlag von Julius Springer, Berlin, Vol. I, 1935, pp. 46 and 47.

(20) Jackson, *J. Chem. Soc.*, **99**, 1066 (1911).

other. The thicker side is more rigid than the thinner, which is stretched by pressure inside the bulb and imparts a lateral motion to the 20-cm. pointer fused to the bottom and terminating in a flattened piece of fine wire. By observing the edge of the wire tip through a long-focus microscope with a reference cross-hair in the eye-piece, pressure differences of 0.5 mm. could be detected. Using this gage as a null instrument, the pressure in the bulb, C, was matched by that in the manometer, upon which it was read.

In carrying out an experiment, the calomel was purified by sublimation *in vacuo*, and finally sublimed into the capsule, B, which was sealed off. After the neck of the capsule was scratched with a file, it was weighed with the calomel, and then slipped into place in the top tube, which was sealed. The whole apparatus was heated for twelve hours to 500° and evacuated through the bottom side-tube, I, to a final pressure so low that the mercury stuck to the top of the capillary of the McLeod gage. The by-pass, F, which protected the gage against rupture during evacuation, was then sealed off. The neck of the sample capsule was broken by means of the glass plunger, A, fitted with a soft-iron core and operated by a solenoid.

An electric furnace was now put over the entire apparatus, so that only the bottom of the gage pointer projected. The furnace was heated gradually, while air was admitted through H to keep the pressure outside the gage equal to that within. When the sample had all volatilized, a series of readings of pressure was made over a range of temperature, measured to 0.25° as before by means of a copper–constantan thermel and potentiometer. Finally the apparatus was cooled, again keeping the pressure equal on both sides of the gage. When the furnace was removed, the by-pass, E, was opened by means of the iron-cored glass plunger, D, and air was admitted to the whole apparatus through H, with equal pressure on each side of the gage.

The weight of the calomel sample was determined by collecting and weighing the bulb and stem and subtracting this weight from that of the bulb and sample. The volume of the bulb, C, (and the connecting tubes filled with calomel vapor during the experiment) was found by weighing the apparatus empty and then filled with water at a known temperature. The volume at the mean temperature of the experiments (400°) was calculated by means of the temperature coefficient of cubical expansion of Pyrex glass[21] 9.6×10^{-6} deg.$^{-1}$. The results of these experiments, presented in Table II, show an average value of 236.3 for the molecular weight of calomel vapor, with an extreme deviation of ±1.7%. The maximum experimental uncertainty of the method is estimated at about 2.5%; hence these results indicate, within experimental error, the formula HgCl (or $Hg + HgCl_2$) for calomel at 375–425°.

These conclusions agree with the results of all other workers except Baker. Since our method of drying the calomel was more vigorous than his, we are at a loss to explain his results, indicating the double formula Hg_2Cl_2, which he attributes to the absence of moisture.

Acknowledgments.—It is a pleasure to acknowledge our indebtedness to Professor Russel A. Fisher of the Physics Department of Northwestern University for his kindness in discussing different phases of this problem with us and in allowing us to use the microphotometer in the study of our absorption plates. We are also grateful to Professor H. Sponer of the Physics Department of Duke University for her courtesy in reading this manuscript and in bringing to our attention some of the calculations of heats of formation which we have included.

Summary

The presence of mercury in calomel vapor was studied by means of the absorption of the resonance line at 2537 Å.

The vapor of undried C. P. calomel shows the presence of mercury at temperatures from 450 to 100°. The partial pressure of the mercury is about half the vapor pressure of the calomel, indicating that it decomposes completely according to the equation $2HgCl = Hg + HgCl_2$. This agrees with the results of Smith and Menzies at 360–400° and with the conclusions Sponer has drawn from the heats of formation.

The vapor of carefully dried calomel shows mercury only at temperatures from 400 to 250° and not below. Similarly, calomel sublimed *in vacuo* at 200° and condensed upon a target cooled with liquid air, shows no trace of mercury, although a mixture of mercury with excess mercuric chloride, sublimed in the same way, showed mercury in the deposit. The vapor of carefully dried calomel also differs from that of the undried C. P. calomel since it exhibits a general absorption in the ultraviolet, starting a little below 3000 Å., which the undried calomel does not show.

The vapor density of carefully dried calomel, measured in an all-glass apparatus at temperatures of 375 to 425° corresponds to the formula HgCl (or $Hg + HgCl_2$). We find no evidence of the existence of the double molecule Hg_2Cl_2 at these temperatures.

EVANSTON, ILLINOIS

RECEIVED APRIL 7, 1937

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[21] "I. C. T.," Vol. II, p. 93.