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STUDIES IN VAPOR PRESSURE, VI: A QUANTITATIVE STUDY OF THE CONSTITUTION OF CALOMEL VAPOR.

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Numerous determinations of the vapor density of calomel at atmospheric pressure have shown, within the limits of error of the methods, that the density corresponds to the formula HgCl. Odling[1] was the first to show, by the amalgamation of a gold-leaf dipped in the vapor, that free mercury was present. The vapor was, therefore, at least partly composed of a mixture of $Hg + HgCl_2$, in equimolecular proportions, which would have the same density as HgCl. Debray[2] could find no amalgamation at 400°, but Brereton Baker[3] obtained it at 445°. Erlenmeyer[4] condensed the vapor rapidly on a tube filled with cold mercury, but found less than 0.03 g. of free mercury in the large deposit of sublimed calomel. Debray secured a similar result with a gilded, silver U-tube containing running water. The presence of free mercury was therefore established, but the evidence, so far as it went, demonstrated only a small amount of dissociation.

Harris and V. Meyer,[5] after confirming by a number of determinations the value of the vapor density previously accepted, attempted in two ways to ascertain the amount of dissociation. In the first place, by heating calomel at about 465° in a porous vessel enclosed in a wider glass

[1] *J. Chem. Soc.*, 3, 211.
[2] *Compt. rend.*, 83, 330.
[3] *J. Chem. Soc.*, 77, 646.
[4] *Ann.*, 131, 124.
[5] *Ber.*, 27, 1842 (1894).

tube, they secured, by diffusion, a "dense mass" of free mercury in the cold part of the outer tube and a "considerable amount" of corrosive sublimate in the residue remaining in the porcelain cell. They infer that this proves "copious dissociation" in calomel vapor. It is obvious, however, that a very small degree of dissociation in the vapor would account for this result equally well. The exit of the mercury through the pores would be expected to disturb a state of equilibrium between the undissociated calomel and the dissociation products, and to result in the final liberation of a far larger proportion of mercury than that contained in the original vapor. This experiment, and another of a similar nature, therefore, in reality only confirmed Odling's proof that some free mercury was present, without in the least degree indicating its amount. The question whether the proportion of undecomposed HgCl in the vapor was over 90 per cent. or zero remained unanswered.

The experiment just described being of a physical nature, Harris and Meyer sought confirmation by chemical means of the (unwarranted) conclusion they had drawn from it. They assume that a vapor largely composed of HgCl should give the reactions of a mercurous salt, while one composed largely of Hg and $HgCl_2$ should give the reactions of a mercuric salt. A rod coated with solid caustic potash, and preheated in an empty test tube (240–260°), was quickly immersed in the vapor of calomel contained in another tube at the same temperature. A yellowish red layer of mercuric oxide appeared immediately. The authors recognize the fact that mercurous oxide is unstable at this temperature, but seem to think it would necessarily have been formed *as a transient stage* if HgCl had been present. They smeared a similar rod with mercurous oxide and, preheating being out of the question, dipped it, cold, into the calomel vapor. After a "long (*geraumer*) time—15–25 seconds," the color changed to yellow owing to the decomposition of the oxide into Hg + HgO. The conclusion drawn from these two experiments is that, since not even a trace of transient darkening was observed with the potash, the mercuric oxide could not have arisen from previously formed mercurous oxide, but must have been the direct product of interaction with the calomel vapor. This mild inference is doubtless correct. But the following clause, stating that the vapor therefore contains the combined mercury as mercuric chloride, indicates complete confusion of thought. Since mercurous oxide is unstable at 240–260°, why should its formation be counted upon under any circumstances at this temperature? True, metastable substances are sometimes produced, but more often they are not. In this case, certainly, the deposition of mercuric oxide would be quite as natural with a vapor wholly composed of a mercurous compound as with one wholly composed of a mercuric salt.

On an experimental foundation which, to say the least, is thus eminently inconclusive, the authors base their final statement: "In vaporizing, calomel decomposes completely according to the equation $Hg_2Cl_2 = Hg + HgCl_2$." This conclusion, that no HgCl is contained in the vapor, by reason of the confidence with which it is stated, has been very generally accepted, and is the view universally held by chemists. Since it was published, no further investigation of the matter seems to have been made. The controversy with Fileti[1] which arose out of this paper, added nothing regarding the possibility of the presence of calomel, as such, in the vapor. It did draw from V. Meyer the statement that he had "never made the mistake of holding that *his experiments* with calomel furnished proof of the double formula," but we are not here concerned with the left-hand side of the equation quoted above. It afforded, also, additional proofs that V. Meyer did not fully understand the principles of chemical equilibrium involved in the problem he had undertaken to solve.

The important fact discovered since V. Meyer's work is that noted by Brereton Baker (*l. c.*), namely, that, in the vapor of *carefully dried* calomel, a gold leaf is not amalgamated. If this observation could be accepted as proving the entire absence of free mercury from the vapor, it would demonstrate conclusively the presence of HgCl, at least in the vapor of the dried substance. This inference follows from the fact that the density of Hg_2Cl_2 is 16.26 (air = 1), while the mean of Baker's measurements with dried calomel is only 15. Thus, if there was no dissociation into $Hg + HgCl_2$, two molecules in every 13 (or 15.4 per cent. of the total molecules) were HgCl. We have seen, however, that the gold-leaf test is uncertain, and it would therefore be unsafe to draw any such conclusion.

An examination of the literature thus reveals the fact that, at the present time, no experimental data exist on which can be based an inference, or even a guess, in regard to the proportion of dissociated (Hg + HgCl) to undissociated (HgCl) molecules in calomel vapor.

Theory of the Method Used to Solve the Problem.—The inconclusiveness of the previous investigations is due chiefly to two facts, namely, that the problem is a quantitative one, while the experiments directed to its solution were all qualitative, and that the experiments and the reasoning applied to the observations were ill considered. If we assume for the present that a polymolecular form of calomel (say Hg_2Cl_2) is present in the vapor only in negligible amounts, or is absent entirely, as the vapor density determinations seem to show, then there are at most three substances present in the vapor, namely HgCl, Hg, and $HgCl_2$. Their relations in the *saturated* vapor, when solid calomel is in equilibrium with the gases, is shown by the following scheme of equilibria:

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[1] Fileti, *Gazz. chim. ital.*, 11, 341 (1881); *J. prakt. Chem.*, [2] 50, 222; 51, 197. V. Meyer, *Ber.*, **27**, 3143; **28**, 364.

$$\text{Calomel (solid)} \rightleftarrows 2\text{HgCl (vapor)} \rightleftarrows \text{Hg} + \text{HgCl}_2.$$

There are three unknown quantities, namely the partial pressures of HgCl, of Hg, and of $HgCl_2$. Three independent observations are required, theoretically, for the measurement of the values of these three quantities at a given temperature. The three observations which appeared to be most suitable were:

1. The vapor pressure of calomel, $P_{\text{calom.}}$ This gives the total value of the three partial pressures.

2. The joint vapor pressure of a mixture of calomel and mercury, with both substances in excess, $P_{\text{mixt.}}$

3. The vapor pressure of mercury alone, $P_{\text{merc.}}$

The results of these three measurements are related in such a way that, with the help of the fundamental laws of chemical equilibrium, the three partial pressures may be calculated from them. It is more convenient, however, to handle the resulting data in another way, namely, by considering first the two extreme cases.

If we first assume the proportion of free mercury in calomel vapor to be exceedingly small, and the dissociation therefore to be negligible, then the vapor of calomel is essentially composed of HgCl, and the relation between the observed data is simple. Each single substance (Exps. 1 and 3), at a fixed temperature, gives a fixed vapor pressure. The concentration of the vapor, which determins the vapor pressure, cannot be permanently altered so long as the solid, or liquid, phase is present. In the mixture (Exp. 2), if the liquid mercury and the solid calomel are immiscible, as they appear to be (see, however, below), and if there is no chemical interaction between their vapors (and there is none), and if the vapors have no component in common (a condition fulfilled in that absence of dissociation which we are for the moment assuming), then the vapor pressure of the mixture must be sensibly equal to the sum of the vapor pressures of mercury and of calomel as measured separately at the same temperature, that is:

$$P_{\text{mixt.}} = P_{\text{merc.}} + P_{\text{calom.}} \tag{1}$$

If, on the other hand, we assume that the dissociation is complete, then HgCl is absent from the vapor: Calomel (solid) $\rightleftarrows$ Hg + $HgCl_2$, and the vapor pressure of calomel (Exp. 1) is made up of only two partial pressures:

$$P_{\text{calom.}} = p_{\text{merc.}} + p_{\text{corros.}}$$

In this instance, with the mixture (Exp. 2) the mercury and the calomel both furnish mercury vapor, but the fact that the latter is also giving off mercury does not cause a permanent increase in the total concentration of mercury vapor beyond that which mercury by itself can give. The partial pressure of mercury vapor in the mixture is fixed by the presence of the free, liquid mercury at a value identical with the vapor pressure of mercury in the absence of calomel at the same temperature. Hence:

$$P_{\text{mixt.}} = P_{\text{merc.}} + p'_{\text{corros.}} \qquad (2)$$

Here the partial pressure of corrosive sublimate in the mixed vapors is determind by the chemical equilibrium between the dissociation products of calomel. Now with pure calomel:

$$p_{\text{merc.}} = p_{\text{corros.}} = \tfrac{1}{2} P_{\text{calom.}}$$

and the value of the calomel dissociation constant is:

$$p_{\text{merc.}} \times p_{\text{corros.}} = \text{const.} = (\tfrac{1}{2} P_{\text{calom.}})^2.$$

In the mixture, the constant, and therefore the product of the partial pressures, must have the same value, so that:

$$P_{\text{merc.}} \times p'_{\text{corros.}} = (\tfrac{1}{2} P_{\text{calom.}})^2$$

and

$$p'_{\text{corros.}} = (\tfrac{1}{2} P_{\text{calom.}})^2 \div P_{\text{merc.}}$$

Hence, substituting in equation 2, the vapor pressure of the mixture is:

$$P_{\text{mixt.}} = P_{\text{merc.}} + \frac{(\tfrac{1}{2} P_{\text{calom.}})^2}{P_{\text{merc.}}} \qquad (3)$$

Thus the vapor pressure of the mixture can be calculated (equation 1 for no dissociation, equation 3 for complete dissociation) from the vapor pressures of calomel and mercury measured separately, and can also be observed directly. If either of these extreme cases represents the facts, then the agreement of the calculated with the observed data will show which assumption is correct.

It will be noted that the assumption that the dissociation is negligible gives the greatest value for the total pressure for the mixture. The assumption that the dissociation is complete gives the minimum value for the same total pressure. If HgCl is present, a value between these two will be found. In case intermediate values are obtained, then the partial pressure ($p_{\text{calom.}}$) of undecomposed calomel, HgCl, can be calculated from the relation:

$$p_{\text{calom.}} = P_{\text{calom.}} - 2\left[P_{\text{merc.}} \pm \sqrt{(P_{\text{mixt.}} - P_{\text{calom.}})\, P_{\text{merc.}}}\right], \qquad (4)$$

of which equation 3 is the particular case when $p_{\text{calom.}} = 0$.

At the time, about ten years ago, when this mode of solving the problem first presented itself to one of us, no suitable and simple method of measuring vapor pressures was known, and a higher degree of accuracy was required than any of the known methods seemed to possess at the vaporizing point of calomel. Methods involving confinement over mercury were excluded, because the value of the vapor pressure of calomel in the absence of mercury was required. Ramsay and Young's dynamic method was not sufficiently accurate, as their results with a dissociating solid of similar volatility—ammonium chloride[1]—showed. The spiral gage alone seemed applicable, but the difficulties connected with its use were deterrent. It was with the object of finding simple methods, applicable to solids and to difficult cases, and at the same time accurate enough to be employed in quantitative chemical work, and therefore suitable for the solution of the calomel problem, that the whole study of methods of determining vapor pressures was undertaken. These methods have already been described. Of the three vapor pressures, a knowledge of which was required, only that of mercury had been measured. But the data given by different observers were so discordant that a redetermination of even these values[2] was necessary.

The Vapor Pressures of Calomel.—The vapor pressures of calomel[3] were determined with the static isoteniscope, using the mixture of potassium and sodium nitrates as the confining fluid, as well as in the bath. The isoteniscope, platinum resistance thermometer, and the other parts of the apparatus, and the manipulation, and the corrections and precautions employed, were all identical with those described in connection with the work on water[4] and used again in the work on mercury (*l. c.*).

The slow interaction with the nitrates of the mercuric chloride in the vapor results in the gradual production of a slight precipitate of mercuric oxide. But the presence of this precipitate in no way interferes with the use of the liquid as a confining fluid. On the other hand, the resulting accumulation of a slight excess of mercury in the vapor, since it occurs at a point remote from the calomel in the bulb, does no harm. Diffusion of this mercury back into the bulb and its penetration to the surface of the calomel would be required in order that it might disturb the equilibrium and affect the vapor pressure. The excess of mercury is formed so slowly, and the diffusion of mercury vapor is in itself so very slow, that prolonged waiting would be required for the development of any effect. Hence, even if the method did not provide, as it does provide, for the complete expulsion of all the accumulated vapor, and its replacement by a fresh supply, immediately before each reading, no slow increase in pressure would arise from this cause. In point of fact, none was ever observed.

The dynamic isoteniscope[5] would have been selected, instead of the static one, but for the fact that to secure strictly comparable results it was desirable to employ static methods for all three determinations.

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[1] See this series, No. 5, THIS JOURNAL, **32**, 1454 (1910).

[2] This series, No. 4, THIS JOURNAL, **32**, 1434 (1910).

[3] Previous measurements by E. Wiedemann and Stelzner, *Ber. deut. physik. Ges.*, **3**, 159 (1905), from 90–180°, by a dynamic method which they used also for iodine; criticized, this series, No. 3, THIS JOURNAL, **32**, 1414.

[4] This series, No. 3, THIS JOURNAL, **32**, 1419 (1910).

[5] This series, No. 5, THIS JOURNAL, **32**, 1448 (1910).

Had the interaction with the nitrates been more rapid, or the vapor more swiftly diffusible, the use of the dynamic form of apparatus would have been necessary for exactness.

The observed vapor pressures are reduced to mm. of mercury at 0° and the sea level at 45° latitude. The temperatures are on the thermodynamic scale, assuming the sulphur boiling point as 445°:

t.	p.	t.	p.
361.82	454.7	388.11	866.7
371.07	563.7	403.79	1229.7
380.41	724.6		

The values at every 5°, obtained by graphic interpolation, are given in the table towards the end of this paper. The boiling point (760 mm.), taken from the curve, is 382.5°.[1]

The Vapor Pressures of a Mixture of Calomel and Mercury.—The vapor pressure of the mixture was not observed directly, because a small error in temperature would have caused an error of many millimeters in the pressure. Instead, we measured the difference in pressure between the mixture and pure mercury, and small changes in temperature cause very slight alterations in this difference. The observed difference was then added to the vapor pressure of mercury at the same temperature. The chief source of error in the resulting observed pressures of the mixture lies, therefore, in the values of the vapor pressures of mercury. Now, the latter enter also as the chief term in the calculated pressures of the mixture, and in the final comparison of observed and calculated pressures of the mixture this error, therefore, largely disappears.

To accomplish the measurements of the difference, two static isoteniscopes, one containing pure mercury and the other containing the mixture, were immersed together in the bath, and were manipulated simultaneously. One was connected with the gage in the usual way. By means of a bent glass tube fused on to the long, open limb of the gage, the other isoteniscope was connected with the other side of this instrument. The pressures acted against one another, through the gage, and only the differences in pressure was shown.

In this instance, since there was free mercury mixed with the calomel, there was no objection to the use of mercury as the confining fluid. Hence, mercury was used as the confining liquid in both isoteniscopes.

The observed differences in pressure were as follows:

t.	p.	t.	p.
326.7	13.0	386.3	94.4
356.6	36.7	393.9	118.5
374.9	66.8	397.8	135.5

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[1] Jonker, *Chem. Weekblad.*, 6, 1035 (1909), finds 373°; Harris and Meyer, *Ibid.*, find 357°.

The following table gives the values of these differences at every 5°, obtained graphically, together with the vapor pressures of the mixture, secured by adding these differences to the vapor pressures of pure mercury at the same temperatures:

t.	Diff. ($P_{\text{mixt.}}$ —$P_{\text{merc.}}$).	$P_{\text{mixt., obsd.}}$	t.	Diff. ($P_{\text{mixt.}}$ —$P_{\text{merc.}}$).	$P_{\text{mixt., obsd.}}$
360°	41.0	843.6	385°	90.8	1321.7
365	48.2	924.9	390	105.7	1441.4
370	56.8	1013.0	395	123.7	1570.8
375	66.8	1108.4	400	147.3	1713.4
380	78.1	1211.1			

An Unexpected Complication of the Problem.—In order that the purpose of the experiments next to be described may be understood, a preliminary examination of the foregoing results is necessary. At 390° (data in final table), for example, the vapor pressure of mercury alone ($P_{\text{merc.}}$) is 1335.4 mm. and that of calomel ($P_{\text{calom.}}$) is 906 mm. Assuming complete dissociation, and substituting in equation 3,

$$p'_{\text{corros.}} = \frac{(\frac{1}{2}P_{\text{calom.}})^2}{P_{\text{merc.}}} = \frac{453^2}{1335.4} = 153.7 \text{ mm.},$$

we obtain 153.7 mm. for the partial pressure of the mercuric chloride vapor in the mixture at 390°, as calculated, with the aid of the theory, from the vapor pressures of the substances observed separately. The directly observed value of the vapor pressure of mercuric chloride at this temperature, which, again assuming complete dissociation, is the difference between the vapor pressures of the mixture and of mercury alone, is only 105.7 mm. (see table above), a discrepancy of over 30 per cent.

The discrepancy is in an unexpected direction. The total pressure of the mixture, calculated on the assumption that there is no dissociation (equation 1) is 1335.4 + 906 = 2241.4 mm., and calculated on the assumption that dissociation is complete is 1335.4 + 153.7 = 1489.1. The observed pressure of the mixture is 1335.4 + 105.7 = 1441.1. If HgCl were present in the vapor, the total pressure would lie at some point between the two calculated values. The observed pressure is *lower* than the smaller of the two, and below the minimum indicated by the theory as thus far considered. HgCl certainly appeared to be proved absent, but before definitly drawing this conclusion it was desirable to account, if possible, for the lack of agreement between the calculated and observed values. A discrepancy of 48 mm. in a total of 1441 mm., or 3.3 per cent., is not unusual in vapor pressure measurements at high temperatures. But the precautions taken and the tests of the method which had been made, rendered it certain that the errors of observation were of nothing like this magnitude. The cause evidently lay in the nature of the substances.

The Density of Saturated Mercury Vapor.—In the first place, it will be noted that the laws of chemical equilibrium employed hold for the actual concentrations of the substances concerned. The *pressures* are substituted in the formulas, on the assumption that they are proportional to the molecular concentrations. Now, that assumption, which is equivalent to assuming that the substances have normal vapor densities, may not be correct in the particular cases under consideration. For example, it was possible that saturated mercury vapor might have an abnormally high vapor density, and that this substance, while being present in the molecular concentration required by the theory of chemical equilibrium, exercised a pressure less than that proper to its concentration. Thus, in the equation from which the partial pressure of mercuric

$$\frac{(\frac{1}{2}P_{\text{calom.}})^2}{P_{\text{merc.}}} = p'_{\text{corros.}},$$

chloride is calculated, the actual concentration of the mercury may be correct, but its pressure (in the denominator) may be too small. This would account for the calculated value of the whole expression being 153.7 mm., while the observed pressure of $HgCl_2$ is only 105.7 mm. That the density of the saturated mercury vapor should be thirty per cent. too high seemed unlikely, but some considerable part of the divergence might originate here.

The only published determinations of the density of saturated mercury vapor seem to be those of Jewett.[1] His work, however, only shows that the density is approximately normal. A divergence of four per cent. would not have been detected with certainty. Then, too, his observations only extended up to 325° where the vapor pressure is about half an atmosphere, and the divergence, if it existed, might be greater at the pressures of nearly two atmospheres occurring in these experiments. Some measurements were, therefore, made at 360 to 400° (pressures 800–1565 mm.). Jewett's method was used, with modifications in the apparatus calculated to insure a degree of accuracy of ±2 per cent., which was sufficient for the present purpose. The divergence was found to be only about 1 per cent. Hence, within the limits of accuracy of the method, the density is normal under these conditions. This hypothesis, therefore, would not account for divergence encountered in the calomel problem.

As the vapor density of saturated mercury vapor is worth studying on its own account, it is proposed to make a more accurate series of measurements in the near future.

The Density of Saturated Calomel Vapor.—Since the vapor pressure of the calomel enters into the numerator of the fraction, any abnormality

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[1] *Phil. Mag.*, [6] 4, 546 (1902).

in the density of the saturated vapor of this substance would involve a correction which would only increase the divergence of which an explanation was being sought. At the same time, the assumption, that concentration and pressure were proportional to one another, was so fundamental to the whole investigation that it seemed necessary to test it in each case.

The vapor density of saturated calomel vapor has never been determind. In the vapor density measurements of Mitscherlich (508°), Deville and Troost (445°), and V. Meyer and Harris (445° and 518°), made at atmospheric pressure, the vapor was much less than half saturated.

For the determination, a small bulb containing a known weight of calomel was fused on to the neck of a round-bottom flask, after the neck of the latter had been drawn out to a capillary and bent downwards (Fig. 1). The flask was exhausted to less than 0.01 mm. pressure through a side tube, which was then sealed off. The whole was immersed in a vigorously stirred bath of the melted nitrates of potassium and sodium, and the temperature was slowly raised to 352.5°, where it was maintained for ten minutes. The bulb was then raised so that, as the highly arched capillary tube emerged from the surface of the melt, it encountered a blowpipe flame which sealed the capillary. The method of sealing the communication between the bulb and the flask is very essential and was adopted after previous experience had shown that cooling the whole apparatus with this tube open (after the manner of Jewett's experiments with sodium) gave rise to slightly variable results. This variability was due, doubtless, to distillation, caused by unequal rates of cooling of the two very dissimilar parts of the apparatus. The weight of the calomel vapor was determind by finding the loss which the amount in the small bulb had sustained. The volume of the flask was measured by weighing full of air and of water, with reduction to vacuum, and was corrected for the expansion of the glass at 352°. The temperature was ascertained with a nitrogen-filled mercury thermometer[1] and was fully corrected. The vapor pressure of calomel, as determind with the same instrument, was therefore employed (352 mm. at 352.5°). The measurement is accurate within less than ±2 per cent., which was sufficient for the purpose. The densities were: observed 0.002169, calculated 0.002125, and their ratio 1.02. The density was therefore normal, within the errors of measurement.

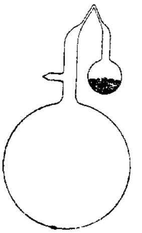

Fig. 1.

Other measurements of the density of saturated calomel vapor have since been made for another purpose, and will be published in another paper. The values confirm the conclusion that the density is normal.

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[1] The thread was almost completely immersed.

The Density of the Mixed Vapors.—Since it thus appeared that the densities of the substances, when separate, were normal, it followed that the main divergence was due to some factor affecting the vapor pressure of the mixture, and such as to make the observed value nearly 4 per cent. lower than the calculated value. It seemed possible that, although the substances when separate showed normal vapor densities, yet when mixed they might influence one another so as to cause the mixture to have an abnormally high density, and therefore an abnormally low vapor pressure. The density of the mixed vapors was therefore determind, using the same methods as for calomel, excepting that two bulbs were attached to the flask, one for each substance. As the data are not of permanent value, the details of the experiments and calculations need not be given. It is sufficient to say that the ratio of the densities found and calculated was 1.02, with an accuracy of ±2 per cent. There was therefore no abnormality which could account for the divergence.

The Solubility of Calomel Vapor in Mercury.—There remained the possibility that, in spite of appearances, calomel might be somewhat soluble in mercury at the temperature concerned. If this turned out to be true, the vapor pressure of the mercury in the mixture would be lowered by the influence of the dissolved calomel, and the total vapor pressure of the mixture would be diminished. A lowering of the vapor pressure of the mercury (1335.4 mm. at 390°) by about 50 mm. would account for the divergence observed. A solubility of the chloride of a metal in the metal itself is not known to occur in many instances, but has been established in the case of bismuth trichloride.[1]

A number of preliminary experiments showed that calomel did dissolve in mercury. They showed also that the complete saturation of a mass of mercury by calomel vapor was an exceedingly slow process even at 360–400°, and that the use of small amounts of mercury, of continual agitation by the vibrations of the stirring apparatus, and of 5–6 hours' time were required for the attainment of the maximum, constant values.[2] The apparatus (Fig. 2) consisted of a small bulb (vol. only 1 cc.) containing a weighed portion of mercury (about 0.5 to 1 g.). The calomel in known amount was contained in a small tube, shown in section and front view in Fig. 2, A. and B. After the calomel tube had been introduced,

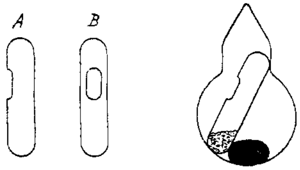

Fig. 2.

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[1] Eggink, *Z. physik. Chem.*, 64, 449.

[2] In the vapor pressure measurements themselves, the fully lowered pressures had been immediately attained. This was doubtless due to the fact that the pressures observed proceeded from the fully saturated surface layer of mercury.

the bulb was exhausted to less than 0.1 mm. pressure and sealed. After the charged apparatus had been heated 5–6 hours at the required temperature, it was opened. The loss in weight of the calomel tube gave the quantity dissolved by the mercury, for the weight required to fill the 1 cc. bulb, as vapor, was negligible. At 398°, for example, three observations gave the following results:

Mercury taken. Gram.	Calomel dissolved.	Parts Hg to 1 pt. calom.
1.3118	0.0622	21.1
0.8796	0.0404	21.8
0.4997	0.0237	21.1
	Mean,	21.33

The possibility that the solubility might be reciprocal, and that mercury might dissolve in calomel, was considered. It was observed that the residual calomel, when cold, was perfectly white and showed no evidence of the presence of mercury. In some of the experiments, also, care was taken to use different relative amounts of calomel and of mercury at the same temperature. A little consideration will show that, in such circumstances, if mercury had been appreciably soluble in calomel, constant results for solubilities, calculated as described above, would not have been obtained. It is clear, therefore, that the solubility of mercury vapor in calomel is too slight to require consideration.

For calculation of the lowering in vapor pressure of the mercury, the solubilities must be expressed in numbers of molecules of each substance. If we take HgCl as the formula of the dissolved calomel, the foregoing value at 398° corresponds to 1 mol. HgCl to 25.11 mols. mercury. If, however, the formula is Hg_2Cl_2, then the ratio becomes 1 : 50.22. If as is conceivable at this high temperature, calomel is unstable, even in solution in mercury, and $HgCl_2$ is the dissolved substance, the ratio is 1 : 51.22. For reasons which will appear presently, the first ratio was taken.

The solubility was measured at three temperatures. The ratios of molecules of mercury to 1 molecule of HgCl found were as follows: 398°, 25.11; 379°, 26.36; 360°, 39.56. These values were plotted, and the solubilities at even temperatures read from the curve are given in the table following.

The Final Results.—From these experiments it is evident that the partial pressure of mercury vapor in the mixture is not that of pure mercury ($P_{\text{merc.}}$), but that of the solution of calomel in the latter (say $P'_{\text{merc.}}$). For example, at 390°, the value is not 1335.4, but a smaller value. At this temperature the molecular solubility is 1HgCl : 25.4Hg. The partial vapor pressure of mercury over this solution is in proportion to the number of molecules of mercury in the total molecules present; that is to say, it is $1335.4 \times 25.4 \div 26.4$, or 1284.8 mm. Substituting this value for $P_{\text{merc.}}$ in equation 3, we obtain $(^1/_2\,906)^2 \div 1284.8$ = partial pressure of mercuric chloride in the mixture = 159.7. This value, plus the vapor pressure of the mercury as lowered by calomel should equal the observed pressure of the mixture: $159.7 + 1284.8 = 1444.5$. The observed pressure of the mixture at this temperature was 1441.4. When the number of measurements involved in the former of these numbers, and the difficulties connected with making exact vapor pressure determinations are taken into account. it will be seen that this agreement within 3.1 mm. in a total of 1444 mm. is much closer than there was any reason to expect. At the other temperatures the degree of agreement is of the same order. It is evident, therefore, that the complete dissociation of calomel vapor, and the absence of HgCl from the vapor, the assumptions underlying equation 3, are satisfactorily established.

The following table contains the complete data. Column 7 shows the vapor pressures of the mixture as calculated by equation 3 from the vapor pressures of calomel (col. 5), and of mercury (col. 4), the latter as depressed by dissolved calomel. Column 8 contains the observed vapor pressures of the mixture. Column 9 gives the differences between the calculated and observed values. The greatest divergence is 6.8, the smallest 0.4, the sum is —0.9, and the deviation of the observations as a whole from the calculated values is only —0.1 mm. It will be noted that, within the range of temperatures covered, the pressure of the mixture has more than doubled itself, but the divergencies show no tendency to progressive change. The average divergence is less than 1 part in 12000. This excellent agreement with the theory that only Hg and $HgCl_2$ are present in the vapor of calomel demonstrates conclusively, within the limits of error of the method, the complete absence alike of HgCl and of Hg_2Cl_2 from the saturated vapor:

1	2	3	4	5	6	7	8	9
t.	Sol'ty $\frac{\text{mols. Hg}}{\text{1 mol. HgCl.}}$	Pmerc.	P'merc., dep. by calom.	Pcalom.	p'corros. calc.	Pmixt., calc. 4+6.	Pmixt., obsd.	Divergence 8-7.
360	39.6	802.6	782.8	434	60.1	843.0	843.6	0.6
365	32.6	876.7	850.6	491	70.9	921.5	924.9	3.4
370	29.3	956.2	924.7	556	83.6	1008.3	1013.0	4.7
375	27.3	1041.6	1004.8	630	98.7	1103.6	1108.4	4.9
380	26.2	1133.0	1091.4	712	116.1	1207.5	1211.1	3.6
385	25.6	1230.9	1184.6	805	136.8	1321.3	1321.7	0.4
390	25.4	1335.4	1284.8	906	159.7	1444.5	1441.4	—3.4
395	25.2	1447.0	1391.8	1017	185.8	1577.6	1570.8	—6.8
400	25.1	1566.1	1506.1	1135	213.9	1719.9	1713.4	—6.5

Calculation of the partial pressures of HgCl, by means of equation 4, leads, of course, to the same conclusion. The values found vary on each side of zero, being for the nine temperatures, 0.9, 4.8, 6.8, 7.0, 5.3, 0.5, —5.3, —10.7, and —10.5 mm. The average of the nine is —0.13

mm., and differs therefore from zero by much less than the errors of measurement.

Results with a Mercury Thermometer.—As the platinum resistance thermometer is a difficult instrument to handle, and is not always available, it is worth while to show that the problem might have been solved and the same conclusion reached with the simplest apparatus. With a good nitrogen-filled thermometer, the actual values of the temperatures between 360 and 400° (and the corresponding pressures) are not exceedingly accurate, as, in spite of careful correction, the individual temperatures taken with such a thermometer may be in error as much as ±1°. But when, as in this case, the same thermometer and the same conditions are used in each of the three series of vapor pressure measurements, the errors partly cancel one another and the results may be useful in spite of them.

In the preliminary experiments, the vapor pressures of mercury, calomel, and the mixture had been determind between 360 and 395° with such a thermometer. The simple, submerged bulblet, vapor pressure apparatus[1] was employed, with a good gage. The solubility measurements given above were the only parts of the better data used in the calculation of the results. The individual values of the pressures, being less accurate, need not be given. The greatest divergence in the final results between theory and calculation was 6 mm. and the smallest 1 mm. The average divergence of the results as a whole from the theory of complete dissociation was only —3.3 mm. Problems of this kind can therefore be solved even by the use of the submerged bulblet apparatus and a mercury thermometer.

The Molecular Weight of Calomel in Solution in Mercury.—In the discussion of the theory of the method it was pointed out that three independent observations were required to demonstrate the constitution of calomel vapor. It turned out, however, that the dimensions of the molecular weight of calomel in solution in mercury was an additional unknown quantity, the presence of which, as a part of the problem, was not foreseen. At least one more independent observation is therefore logically necessary to establish the fact that the dissolved calomel is monomolecular. It will be noted, however, that instead of only three observations, three groups of observations, covering a wide range of pressures, were made. The experimental material is therefore amply sufficient to sustain this additional conclusion.

If we assume, for the moment, that the dissolved calomel is bimolecular (Hg_2Cl_2), the ratios of molecules of mercury to molecules of calomel (col. 2) are all doubled. This alters the proportions of mercury mole-

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[1] THIS JOURNAL, 32, 907. It is worth noting that this method is dynamic, while the one used in the main series was static.

cules to total molecules (*e. g.*, at 390° to 50.8:51.8), and therefore the calculated partial pressures of the mercury in the solution. Figuring on this basis, the final divergencies between calculated and observed data (col. 9) now become —12.2, —9.7, —11.1, —13.5, —18.0, etc., up to —36.6 at 400°. The excellent correspondence thus disappears, and the divergencies increase rapidly with ascending temperature.

Conclusions.—1. A series of vapor pressures of calomel from 360 to 400° has been obtained. The boiling point is found to be 382.5°.

2. It has been shown by a quantitative vapor pressure method (static), that calomel vapor, even when saturated, is wholly dissociated, and that molecules of the classes HgCl and Hg_2Cl_2 are not present.

3. Independent measurements, with an apparatus working on the dynamic principle, lead to the same conclusion.

4. It has been shown that the molecular weight of calomel dissolved in mercury at 360–400° corresponds to the monomolecular formula, HgCl.

5. It has been shown that, by the use of the isoteniscope, chemical problems can be investigated, and results can be obtained, possessing the same order of accuracy that is claimed for the most refined methods of quantitative analysis.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 60.]

TRANSFERENCE EXPERIMENTS WITH THALLOUS SULPHATE AND LEAD NITRATE.

BY K. GEORGE FALK.

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1. Introduction.

In a paper published some years ago, A. A. Noyes[1] pointed out that the change of the transference number of tri-ionic salts with the concentration might be expected to throw light on the question as to whether intermediate ions, such as KSO_4^- in the case of potassium sulphate, or NO_3Ba^+ in the case of barium nitrate, existed in appreciable quantities in solutions of such salts. Results for potassium sulphate, barium chloride, and barium nitrate were published. In this paper, the results obtained with two other salts of this type, thallous sulphate and lead nitrate, will be given; and the theoretical significance of the transference results will be considered.

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[1] THIS JOURNAL, **23**, 37 (1901).