after heating in sealed glass tubes for a few hours at 150°, reaction was complete. As in the case of thionyl chloride and mercuric oxide, when a large excess of reagent was employed, no sulphur dioxide was formed and the tubes were therefore under no pressure. But when only a slight excess was employed, considerable pressure was developed. In both cases a strong odor of sulphur monochloride was noticeable while the crystals were being dried, and the filter paper was colored slightly yellow, evidently by this compound. Reaction probably proceeds according to one of the two following equations, depending upon the amount of thionyl chloride used:

$$Hg + 4SOCl_2 = HgCl_2 + 2SO_2Cl_2 + S_2Cl_2$$
$$3Hg + 4SOCl_2 = 3HgCl_2 + 2SO_2 + S_2Cl_2.$$

When an excess of mercury was employed, mercurous chloride, sulphur dioxide and sulphur monochloride were the products.

The author has heretofore investigated many reactions between thionyl chloride and metals or oxides, but the two above-mentioned reactions, in which a large excess of thionyl chloride was used, are the first he has found in which no pressure is developed or in which sulphur dioxide is not one of the final products. It has not been possible to positively identify sulphuryl chloride inasmuch as the amount of thionyl chloride used was small, and the boiling points of the two liquids are too close to allow of definite tests by fractional distillation of small quantities. However, considering the facts heretofore given, the author has little doubt that the reaction proceeds with the formation of sulphuryl chloride, according to the equations given.

The two reactions with sulphuryl chloride are also noteworthy inasmuch as they are the first reactions found for this reagent in which sulphur trioxide or a sulphate is produced.

FACULTÉ DES SCIENCES DE PARIS.
LABORATOIRE DE CHIMIE GÉNÉRALE.

[CONTRIBUTION FROM THE LABORATORIES OF GENERAL AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF CHICAGO.]

DOES CALOMEL FURNISH ANOTHER CONTRADICTION OF THE THEORY OF HETEROGENEOUS DISSOCIATION EQUILIBRIUM?

BY ALEXANDER SMITH.

Received January 4, 1910.

As is well known, undried ammonium chloride gives, at 360°, values for the vapor density corresponding to the formula ½ NH_4Cl, and indicating complete dissociation. Brereton Baker,[1] however, using the Victor Meyer and the Dumas methods found that the salt, when elaborately dried, gave at the same temperature values corresponding very nearly

[1] *J. Chem. Soc.*, 65, 615; 73, 475.

to the formula NH_4Cl. Since, in each case, to operate the method, about one atmosphere pressure of the vapor was necessary, it is fair to infer that in the first case the undried solid was in equilibrium with a minute partial pressure of the undissociated molecules, while in the second case the dried solid was in equilibrium with something like 760 mm. pressure of the same molecules. Abegg[1] has recently called attention to this anomaly, consisting in an apparent contradiction of the theory of heterogeneous dissociation equilibrium. At his instance, F. M. G. Johnson[2] has measured the vapor pressures of the salt, and established the fact that at about 340° the dried and undried forms of the substance do give undissociated and dissociated vapor, respectively, and yet exhibit equal pressures (amounting to 760 mm.) of the saturated vapors. The existence of the anomaly is therefore demonstrated.

Now Brereton Baker[3] found likewise that dried calomel, at 445°, gave vapor densities corresponding very nearly to the formula Hg_2Cl_2 (average density, 435; theory for Hg_2Cl_2, 470). Yet, as is well known, calomel when undried gives at this temperature vapor densities corresponding to the formula HgCl (or $Hg + HgCl_2$). The purpose of this paper is to point out that calomel appears therefore to exhibit the same anomaly as does ammonium chloride. The inference is, in the case of calomel, to a very slight degree less certain of confirmation, since at 445° calomel gives a vapor pressure of about two atmospheres, and at 760 mm. the vapor is therefore only half saturated and is not in equilibrium with the solid. It seems, nevertheless, probable that, at one and the same temperature, dried calomel will be found to be in equilibrium with 760 mm. pressure of Hg_2Cl_2 molecules, although undried calomel will give the same total pressure, and only a minute partial pressure of the undissociated molecules. Experiments to ascertain whether calomel does actually exhibit this anomaly are now being made in this laboratory.

The matter is of great significance for the explanation of Abegg's anomaly. Among the suggested explanations, the two most plausible are: (1) Abegg's[4] that the heat of formation of gaseous, undissociated NH_4Cl happens to be equal to the heat of dissociation of gaseous NH_4Cl into $NH_3 + HCl$; and (2) Wegscheider's[5] that it is a case of polymorphy, and suspended transformation in the dry sample, accompanied by accidental identity of the high vapor pressure of NH_4Cl molecules from the form unstable at 360° with the vapor pressure of NH_3 and HCl molecules from the form stable at 360°. Either explanation depends on a coincidence

---

[1] *Z. physik. Chem.*, 61, 455.

[2] *Ibid.*, 61, 457.

[3] *J. Chem. Soc.*, 77, 646.

[4] *Z. physik. Chem.*, 62, 608.

[5] *Ibid.*, 65, 97.

which could not occur in precisely the same way with a different substance unless the coincidence was due to some as yet unrecognized general relation, and not to accident.

CHICAGO, December 20, 1909.

THE CONDENSATION PRODUCTS OF MELLITIC ACID WITH META-AMINO PHENOL AND THEIR BEARING ON THE RELATIONSHIP OF COLOR AND FLUORESCENCE TO CONSTITUTION.

BY OSWALD SILBERRAD AND CHARLES SMART ROY.

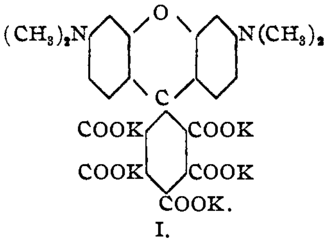
Received November 27, 1909.

In a previous paper by one of the authors on the condensation products of mellitic[1] and pyromellitic acids with resorcinol,[2] much evidence was brought to show that color and fluorescence are not necessarily dependent on quinoidal structure.

The present work deals with the corresponding rhodamines, and fully confirms the conclusions arrived at in the previous paper. Coupled with, and to some extent interdependent on these results is the possibility of ascribing fluorescence to oscillatory tautomerism. As will be shown below it is illogical and impractical to formulate all the compounds dealt with in this paper on the quinone system, and since they are without exception intensely colored and strongly fluorescent, it becomes evident that a quinoidal grouping is not a necessarily integral part of a colored and fluorescent compound.

The compounds dealt with in this paper may be divided into three groups, namely:

1. *Monoxanthyl Derivatives*, of which tetramethyldiaminoxanthylbenzenepentacarboxylic acid may be taken as typical—formula I represents the potassium salt,



I.

2. *Dixanthyl Derivatives*.—These exist in two modifications according to whether the xanthyl groups are para or meta to one another. They behave as tetrabasic acids:

---

[1] The mellitic acid required for this investigation was manufactured from charcoal according to British Patent No. 24,662, '07.

[2] Silberrad, *J. Chem. Soc.*, **89**, 1789 (1906).