

concerned run to completion, the proper equilibrium conditions must be chosen, and any change in these conditions will affect the completeness of the reaction. Such conditions cannot be predicted beforehand but must be subjected to careful experimental determination.

The best conditions for the standardization of a thiosulfate solution, using the various standards studied, may be summarized as follows.

Pure Iodine.—The sample is weighed in a special weighing bottle and titrated in a neutral solution containing 2% of iodide at the end-point.

Permanganate.—The permanganate is added to an acidified solution of potassium iodide, the mixture allowed to stand in the dark for ten minutes and the titration completed: final acidity, 0.1 *M* hydrochloric acid; final concentration of iodide, 6%.

Dichromate.—The dichromate is added to an acidified solution of potassium iodide, the mixture allowed to stand in the dark for ten minutes and the titration completed; final acidity, 0.2 *M* hydrochloric acid; final concentration of iodide, 2%.

Bromate.—The bromate is added to an acidified solution of potassium iodide, and the mixture titrated immediately; final acidity, 0.1 *M* hydrochloric acid; final concentration of iodide, 6%.

In all cases an amount of the substance equivalent to 40 cc. of 0.1 *N* solution and a final volume of 160 cc., have been found very convenient.

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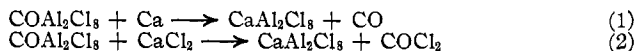
THE PREPARATION OF PHOSGENO SALTS

BY ALBERT F. O. GERMANN AND CHARLES R. TIMPANY

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The properties of solutions of aluminum chloride in liquid phosgene can best be interpreted by regarding the solution as containing an acid, COAl_2Cl_3 , in which the carbonyl group takes the place of hydrogen in the well-known acids.¹ This acid is capable of reacting with metals to yield salts and carbon monoxide, or with metallic chlorides, which are to be regarded as bases typical of this system, to yield salts and phosgene, as set forth in the equations:



The further study of this group of salts made it essential to develop a general method for their preparation in very pure form, and in relatively large amounts. Because of the intolerable odor of phosgene, its high vapor tension, and the readiness with which all of the reacting materials react with water, this had to be done in a closed system, where the internal pressure might attain 2 atmospheres. Reaction 1 would increase this pressure,

¹ Germann, *Science*, **61**, 71 (1925).

because of the carbon monoxide released as a by-product, making the method undesirable, even if pure calcium were obtainable. Reaction 2 was therefore chosen, and was all the more desirable because of the high degree of purity that could be attained in the preparation of the reaction substances and because calcium chloride and other strongly polar chlorides are insoluble in phosgene.

Pure phosgene was prepared from technical phosgene by a method essentially the same as that used in previous researches on phosgene,² and was distilled into the evacuated apparatus. Pure anhydrous aluminum chloride was prepared by distillation, under a pressure of 3 atmospheres, of a sample of the purest obtainable anhydrous chloride mixed with aluminum powder to react with the iron chloride present. The calcium chloride

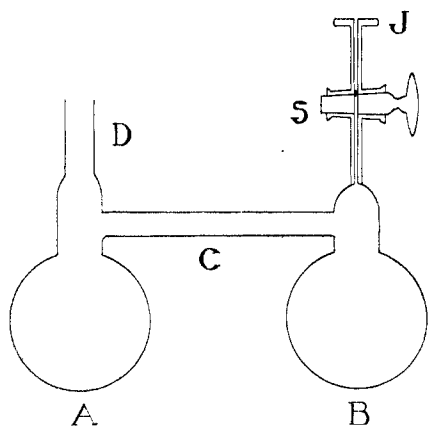


Fig. 1.

was a specimen of the c. p. fused salt, which was further dried by fusion in platinum in a current of dry hydrogen chloride. The apparatus used is shown in Fig. 1. The necks of two heavy-walled Pyrex flasks A and B, of about 250cc. capacity each, were joined by means of the connecting tube C, whose diameter was 10 mm. A Pyrex stopcock S and plane-ground joint J were fused to the neck of B. The apparatus weighed less than 150 g. Forty-one g. of anhydrous calcium chloride was introduced into the thoroughly dried apparatus at D, followed by 54 g. of anhydrous aluminum chloride; the apparatus was then sealed off at D, evacuated, and about 100 cc. of liquid phosgene distilled into it. The stopper at S was securely clamped and the apparatus was allowed to warm to room temperature. The aluminum chloride, which is very soluble, dissolved readily; after the mixture had reached room temperature calcium chloride also began to dissolve, and the heat of reaction was sufficient to raise the temperature appreciably, so that phosgene distilled from A to B. The mixture was allowed to stand for several days to insure complete reaction; the undissolved calcium chloride was then transferred to Bulb B, and the solution to Bulb A. The dissolved salt was crystallized by distilling some of the solvent into Bulb B. The crystallized salt had a distinct amber tinge, showing the presence of impurities, perhaps iron chloride. The mother liquor, which contained the major portion of the impurities, was then decanted into Bulb B. The crystallized salt remaining in Bulb A was washed repeatedly

² Germann and Gagos, *J. Phys. Chem.*, **28**, 965 (1924).

by decantation with fresh phosgene distilled in from B, until no trace of the coloration remained. Finally the salt was dried by distilling the excess of phosgene until the residue partly effloresced, the bulb containing the purified salt was opened, the salt transferred to a tightly stoppered reagent bottle and the whole stored in a desiccator containing calcium chloride to prevent loss of phosgene of crystallization. The yield of purified salt was 52 g., which represents a recovery of about 50% of the crude material.

Published methods for the determination of phosgene are not very satisfactory for the analysis of compounds of this type. After several trials, the following method was developed and proved to be entirely satisfactory. A weighed sample, about 0.5 g., was introduced into the tube illustrated in Fig. 2 through the side tube A, which was then sealed off, and the tube weighed. The gross weight of the tube was corrected for the weight of air contained. The tube was then evacuated, while the sample was warmed at B with a small luminous flame to drive off phosgene of crystallization, as long as gas was evolved, or until the pressure fell to zero. A second weighing gave the weight of phosgene in the sample. For the analysis of the residue, a few drops of water were introduced into A through the stopcock, without the introduction of air; after several hours the sample at B had completely dissolved in this water. More water was introduced and finally the tube was opened at A, and the solution transferred to a beaker, where chlorine, aluminum and calcium were determined gravimetrically in the ordinary way, except that the procedure was shortened by omitting the customary double precipitation of aluminum hydroxide, making the aluminum high due to adsorption of calcium, and the values for calcium correspondingly low. The analysis was not repeated, as the main questions to be settled were the phosgene content, the homogeneity of the sample, and the possibility of driving off all the phosgene by this method, as a statement by Baud regarding the volatility of the compound $4\text{AlCl}_3 \cdot \text{COCl}_2$ made this seem doubtful.³ As the analyses show, this does not seem to have been a disturbing factor. In Table I, Col. A gives the

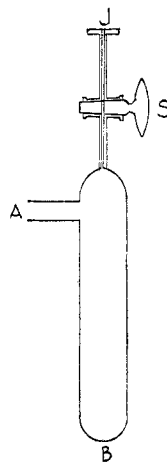


Fig. 2.

TABLE I
ANALYSES

	Sample 1		Sample 2		A	Sample 3 B	Calcd.
	A	B	A	B			
Phosgene, %	25.78	...	25.76	...	25.68
Chlorine, %	54.88	74.89	55.09	74.92	55.24	74.88	75.10
Aluminum, %	11.00	15.01	10.93	14.87	10.97	14.87	14.30
Calcium, %	7.40	10.10	7.51	10.21	7.56	10.25	10.61

³ Baud, *Compt. rend.*, **140**, 1688 (1905).

analysis of the partially effloresced product, while Col. B gives the analysis on a phosgene-free basis.

A repetition of the vapor-tension measurements made by Germann and Gagos has verified the composition of the phosgenate as containing two molecules of phosgene: $\text{CaAl}_2\text{Cl}_8 \cdot 2\text{COCl}_2$. The vapor tension of the phosgenate at 25° , at which the measurements were carried out, is about 40 mm., which agrees with the value 25–30 mm. at 19° , found by them. The solubility of the completely dephosgenated salt at 25° was found to be 33 g. of salt per 100 g. of saturated solution, or 100 g. of the crystallized diphosgenate per 100 g. of solvent.

We wish to thank the Chemical Warfare Service for their interest in this work and for supplies of phosgene.

Summary

A method for the preparation and analysis of phosgeno salts in phosgene solution has been described, with particular reference to the calcium salt; the method is applicable to any soluble salt, not only in phosgene, but in other volatile solvents, where isolation from the atmosphere is essential, and where the pressures developed are not too great.

STANFORD UNIVERSITY, CALIFORNIA

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THIN FILMS OF PLATINUM AND NICKEL AND CATALYTIC ACTIVITY

BY A. W. GAUGER¹

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For some time there has been considerable discussion in the literature as to whether the active material in a nickel catalyst is in reality metallic nickel or an oxide or sub-oxide of some type.² As it is impossible to prepare a nickel catalyst from nickel oxide, which will be completely reduced, the study of this question by direct experiment has been limited to attempts at preparing catalysts from compounds of nickel containing no oxygen. Since the importance of extent of surface has seemed to be so great, the author believed it possible to prepare a finely-divided catalyst which should have an exceedingly large surface and yet by virtue of its method of preparation be entirely free from oxygen or oxide. He proposed to prepare such a material (nickel) and investigate its catalytic activity for the reaction, $\text{C}_2\text{H}_4 + \text{H}_2 \longrightarrow \text{C}_2\text{H}_6$.

¹ National Research Fellow in Chemistry.

² Kelber, *Ber.*, **54**, 1701 (1921). Willstätter and Waldschmidt-Leitz, *Ber.*, **54**, 113 (1921). Boswell, *Proc. Roy. Soc. Canada*, **16**, sect. III (1922).