furous acid upon the sulfites of iron, zinc, and manganese is a double decomposition of the usual type; and (2) that in as far as the conditions of the reaction lead to the oxidation of the liberated hydrogen sulfide by sulfur dioxide, a corresponding quantity of thiosulfate is formed as a secondary reaction.

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ON EXTRACTION WITH LIQUEFIED GASES AND THE AMMONOLYSIS OF HYDRAZINE SULFATE.

BY FRITZ FRIEDRICHS.

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In connection with the choice of a solvent for use in extraction two considerations are of importance: first, the relative solubility of the substances to be separated; and second, the ease with which the solvent may be recovered without loss and without decomposition of the extract or of the residue. Since the removal of the solvent is usually effected by evaporation, a solvent with the lowest possible boiling point would normally be preferable, especially when the material to be extracted decomposes at relatively low temperatures, or possesses a high vapor tension. This leads at once to the application of liquefied gases in extraction in case the usual solvents can not be readily recovered after the operation is complete.

The reason that such comparatively inexpensive gases as ammonia, sulfur dioxide, hydrogen sulfide, methylamine, etc., have not found more frequent application as extracting media in scientific and industrial work lies in the fact that the solvent power of these substances, with the exception of ammonia, has not yet been thoroughly investigated, and further, that suitable apparatus for the purpose has not yet been designed. Various extractions, to be discussed in more detail later, have already been carried out by A. W. Browne, T. W. B. Welsh,[1] and A. E. Houlehan,[2] but the apparatus employed has not yet been completely developed for general use. The author of the present paper, in undertaking the continuation of the work, has consequently devised, on the basis of the work already done, the apparatus shown in the accompanying sketch.

The apparatus consists of three parts: (1) the extraction apparatus proper, D, (2) the container C, for the substance to be extracted, suspended in D from three glass projections, and (3) the condenser B, which is carefully ground to fit D. The extraction apparatus is modeled after the Landsiedl device except that the bulb F is provided with a small siphon and with a stopcock, G, through which the extract may be drawn off, and that the entire apparatus is insulated by means of a vacuum jacket.

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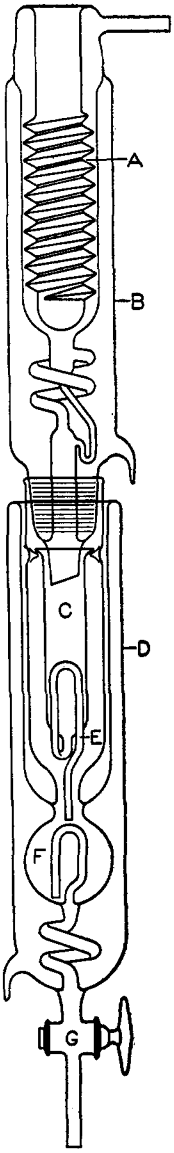
[1] THIS JOURNAL, 33, 1728–34 (1911).

[2] *Ibid.*, 33, 1734–42 (1911).

Between this jacket and the inner part of the apparatus a small quantity of the refrigerant may be introduced. The condenser is of the screw type,[1] the screw itself constituting a receptacle for the refrigerant, and is, like the extraction apparatus, surrounded by a vacuum jacket. In order to permit free delivery of the condensate and free return of the vapors the condenser is equipped with a special device clearly shown in the sketch. It is to be noted that the glass tubes passing through the vacuum jackets are in each case so constructed as to permit thermal expansion or contraction without breaking the apparatus. The upper part of the condenser is provided with an inlet tube for the gas to be liquefied, which is obtained from some convenient source, either a cylinder or a gas generator, and which is suitably purified and dried (in the case of ammonia, for example, by means of a long tube filled with sodium wire). It is advisable also to connect the condenser with a mercury manometer, which serves the double purpose of indicating the pressure in the apparatus, and of acting as a safety outlet.



For the gases already named, solid carbon dioxide and ether may be used as the refrigerant, while for gases with lower boiling points, such as oxygen or methane, liquid air may be employed. When liquid air is used it is advisable to introduce first a small amount of ether into the apparatus and then slowly to add the liquid air, in order to minimize danger of breaking the apparatus. In order to obtain still lower temperatures in the condenser, the screw may be connected with an air pump, and the refrigerant caused to evaporate under reduced pressure.

The apparatus just described has been found to serve admirably in a research upon the ammonolysis of hydrazine sulfate. As already shown by Browne and Welsh, hydrazine sulfate is decomposed by liquid ammonia into free hydrazine and ammonium sulfate in accordance with the equation;

$$N_2H_4.H_2SO_4 + NH_3 \rightleftarrows (NH_3)_2.H_2SO_4 + N_2H_4.$$

The reaction is moreover to be regarded as reversible, inasmuch as Lobry de Bruyn[2] has already shown that free hydrazine can liberate ammonia from ammonium sulfate. Since ammonium sulfate—or rather, in accordance with the hitherto unpublished experiments performed by Mr.

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[1] *Z. angew. Chem.*, **23**, 2425–26 (1910).

[2] *Rec. trav. chim.*, **15**, 179 (1896).

L. J. Ulrich in this laboratory, the triammonate of ammonium sulfate—is entirely insoluble[1] in liquid ammonia, while hydrazine is comparatively soluble, the employment of an excess of ammonia during the extraction displaces the equilibrium toward the right, with the result that quantitative ammonolysis takes place. It was therefore to be expected, as Browne, Welsh, and Houlehan have already intimated, that anhydrous hydrazine might be conveniently prepared by this method.

The hydrazine sulfate used in the following experiments was obtained by precipitation with alcohol from an aqueous solution of a sample of the salt previously purified by four-fold recrystallization. This product was repeatedly washed with alcohol and was finally dried in a desiccator. A weighed sample of this pure white salt was introduced into the vessel C in a Schleicher and Schüll extraction thimble, and after opening the stopcock G, the air was driven from the apparatus by means of ammonia. By filling the tube between the stopcock G and the bulb F with mercury, which is of course a good conductor of heat, it was found possible to supply automatically an amount of heat sufficient to effect continuous evaporation of the liquid ammonia in F. After the salt had become pretty well saturated with ammonia at room temperature, solid carbon dioxide and ether were introduced into the jacket of the extraction apparatus and into the condenser screw A. Ammonia was at once condensed and the extraction began to take place. During this operation the bulk of the salt increased to such an extent that during the earlier experiments the paper thimble, and on one occasion even the vessel C burst, while in another case C became clogged so as to necessitate interruption of the experiment. It was then found that these difficulties could be readily avoided by placing glass wool in the thimble with the salt, by supporting the thimble upon a porcelain Witt plate and by inserting several short pieces of glass tubing between the thimble and the walls of C. When the bulb F had become about three-fourths filled with liquid, the valve of the ammonia cylinder was closed. The operation of the apparatus was then entirely automatic and was surprisingly smooth and uniform, as could be observed from the manometer. As the temperature of the gas that rises from F to the condenser is never higher in the apparatus than the boiling point of liquid ammonia (—33.45° under atmospheric pressure) or of the liquid ammonia solution, the consumption of carbon dioxide is relatively low. During the ammonolysis experiments for example it was found necessary on the average to fill the condenser screw from three to four times for each extraction. After the extraction had been completed the apparatus was allowed to warm up and the gas to escape through the safety outlet. The extract was then drawn off by opening the stopcock G. When it was desired to measure the amount of the extract directly it was of course

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[1] Franklin and Kraus, *Am. Chem. J.*, 20, 820–36, 823 (1898).

necessary to rinse out the bulb F with liquid ammonia. The vessel C containing the residual ammonium sulfate combined with considerable amounts of ammonia in the form of an ammonate was now removed, was left in a desiccator over sulfuric acid until free from ammonate ammonia, and was weighed. The results obtained in several typical experiments are summarized in the subjoined table.

		$(NH_3)_2.H_2SO_4$.			N_2H_4.	
No. of Expt.	$N_2H_4.H_2SO_4$ used. Grams.	Obtained. Grams.	Calculated. Grams.	Per cent of theory.	Obtained. Grams.	Per cent of theory.
1	2.082	2.14	2.11	101.4	...	..
2	2.366	2.42	2.43	99.6	0.529	90.6
3	4.688	4.79	4.76	100.6	0.817	95.9
4	8.377	8.52	8.50	100.2	...	..
		Average of Expts. 2, 3 and 4		100.1		

In Experiments 2, 3 and 4, the presence of hydrazine in the residue could not be detected with the aid of Fehling's solution, nor could the presence of sulfuric acid be shown in the extract. In Experiment 1 several hard lumps of salt containing a considerable amount of hydrazine were found at the bottom of the thimble, indicating that the extraction was not in this case complete. This first experiment was therefore left out of account in calculating the average. The loss of hydrazine was occasioned by the necessity of rinsing out F with liquid ammonia.

From these experiments it is evident, as was to have been expected, that the ammonolysis may be considered to proceed quantitatively under the prevailing conditions. It is further to be concluded that it should be possible without difficulty to prepare anhydrous hydrazine in larger amounts by this method. For this purpose it would of course be advisable to substitute an apparatus built of iron for that of glass. It would then be possible to use ice as the refrigerant, as the apparatus would readily bear a pressure of 4.2 atmospheres. The greater solvent power of liquid ammonia at the higher temperature would undoubtedly be of advantage. Experiments in this direction are now in progress.

It is hoped that this illustration of the application of liquefied gases as extraction media will call the attention of other investigators to this field of work, and that the apparatus described herewith may be of service in carrying out further experiments.

In conclusion the author wishes to express his gratitude to Professor A. W. Browne, who has suggested the present investigation, and to the firm of Greiner and Friedrich, Stützerbach, Germany, by whom the apparatus has been constructed.

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