

### Summary

The precipitation of zinc sulfide from sulfate-hydrosulfate solutions has been studied. The precipitation was found to be complete to less than 0.25 mg. out of 257 mg. at a hydrogen-ion concentration as high as  $2.5 \times 10^{-2}$ . Nickel, iron, manganese, chromium and aluminum may be separated quantitatively from zinc by this sulfide precipitation, but cobalt cannot be so separated. High chloride-ion concentration increases the solubility of the zinc sulfide. A procedure is outlined for the quantitative precipitation of zinc and its separation from the other metals. Methods of igniting the precipitate have been studied. The temperature should be closely controlled at  $500^\circ$  when igniting the zinc sulfate, and at  $900^\circ$  when igniting the sulfate to oxide.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

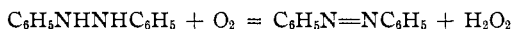
## THE DIRECT PREPARATION OF HYDROGEN PEROXIDE IN A HIGH CONCENTRATION

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The fact that hydrazobenzene is readily autoxidized with the formation of hydrogen peroxide has been pointed out by Manchot and Herzog.<sup>1</sup> In an investigation carried out in this Laboratory it was found that in an alcoholic solution the reaction is practically quantitative according to the equation



As would be expected a small amount of the alcohol is oxidized by the hydrogen peroxide. The reaction takes place very readily in either ethanol or propanol. By dissolving hydrazobenzene in alcohol and bubbling oxygen through the solution it is possible to follow the speed of reaction by measuring colorimetrically the increasing color of the solution caused by the formation of the azobenzene. The reaction apparently takes place between the dissolved oxygen and the hydrazobenzene, so that in studying the speed of the reaction it is necessary to bubble the oxygen through the solution fast enough to keep the solution saturated. The reaction is bimolecular as evidenced by the following data taken from a series of experiments.

Temp., $30^\circ$ ; 1% solution of hydrazobenzene in 95% $\text{C}_2\text{H}_5\text{OH}$			
$t$ , min.	$a - x$	$x$	$k \times 10^4$
0	33.1		
16	20.6	12.5	11.4

<sup>1</sup> Manchot and Herzog, *Ann.*, **316**, 331 (1901).

<i>t</i> , min.	<i>a</i> - <i>x</i>	<i>x</i>	<i>k</i> × 10 <sup>4</sup>
26	17.0	16.1	11.0
36	14.5	18.6	10.8
46	12.2	20.9	11.3
62	10.8	22.3	10.1
105	6.6	26.5	11.5
		Av.	11.0

In the experiment recorded the oxygen was released at the bottom of a Nessler tube containing 50 cc. of solution, through a delivery tube with an opening of about 1 mm. In another experiment with a delivery tube opening of 2 mm. bore the value of  $k \times 10^4$  was 10.6, when the oxygen was passed through a group of five small jets of 0.5 mm. each, the constant was 9.7. Oxygen was bubbled through these delivery tubes without regard to the absolute rate, the object being to keep a rapid stream of bubbles flowing from each jet. The fact that the constants agree shows that the reaction is taking place in solution and not at the gas-liquid interface. The reaction when carried out in a tube covered with tin foil gave a constant of 10.2 showing that diffused light has no appreciable effect. In absolute ethyl alcohol the constant had a value of  $3.4 \times 10^{-4}$  while in isopropyl alcohol the speed of oxidation was somewhat slower,  $4.2 \times 10^{-5}$ .

**Autoxidation in Benzene Solution.**—In an effort to isolate an intermediate product of the peroxide type, the hydrazobenzene was oxidized in benzene solution. The concentration of the oxygen in the solution was increased by placing it in a bomb, lowering the temperature to 0° and increasing the oxygen pressure to about 370 pounds per square inch. No intermediate compound could be detected. However, drops of liquid separated from the benzene solution, which when analyzed were found to be hydrogen peroxide of a purity of about 94%. The total yield of hydrogen peroxide was determined and it was found that from a given weight of hydrazobenzene it was possible to obtain about 97% of the theoretical yield of hydrogen peroxide.

This quantitative yield of highly concentrated hydrogen peroxide from hydrazobenzene suggests the possibility of production of the peroxide on a large scale. Its attractive feature, of course, lies in the fact that the azobenzene formed in the reaction can be changed to hydrazobenzene and thus used continuously. The problem is the subject of further investigation.

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