

where  $d_p$  is the density of the gas at pressure  $p$  and temperature  $T$ , and  $d_0$  is the density of the gas at atmospheric pressure and at temperature  $T$ .

I wish to express my appreciation to the entire staff of the Fixed Nitrogen Research Laboratory for unstinted coöperation in solving the many problems involved in this investigation. I am especially indebted to Dr. J. A. Almquist for counsel and advice, to Dr. H. L. Cupples for assistance in the tedious mathematical computations and to my assistant, Mr. T. H. Tremearne, for his untiring and efficient help.

### Summary

The compressibility factors at 0° for pure hydrogen, pure nitrogen and eight mixtures of these gases have been determined through a pressure range of 1000 atmospheres.

The compressibility factor of a mixture of the two gases is not a linear function of its composition. A maximum positive deviation of 1.9% was observed in a mixture containing 60% of hydrogen at 200 atmospheres pressure. A maximum negative deviation of 0.55% appears in a mixture containing 25% of hydrogen at 1000 atmospheres' pressure.

The densities of pure nitrogen, pure hydrogen and eight mixtures of these gases at nine pressures have been calculated. Densities range from 0.08982 g. per liter for pure hydrogen at 1 atmosphere to 605.4 g. per liter for pure nitrogen at 1000 atmospheres' pressure.

Empirical equations relating gas composition and compressibility have been derived and certain working formulas presented.

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[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY OF NEW YORK UNIVERSITY]

## THE DIRECT OXIDATION OF LITHIUM IODIDE

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Many anhydrous inorganic halides, when heated in a current of oxygen, have been observed to undergo change, resulting in the formation of metallic oxides and the liberation of free halogen.<sup>1</sup> Potassium chloride, bromide and iodide, when heated in a stream of air or oxygen to a temperature of about 500° form, respectively, traces of chlorate, bromate and iodate simultaneously with the liberation of small amounts of free halogen.<sup>2</sup> In the investigations mentioned above, the experiments have apparently been but qualitative in nature, no data being given as to the amount of oxide, oxygenated salt formed, or of the halogen evolved.

<sup>1</sup> Schulze, *J. prakt. Chem.*, [2] 21, 407 (1880).

<sup>2</sup> (a) Berthelot, *Bull. soc. chim.*, [2] 28, 495 (1877). (b) Pettersson, *Z. anal. Chem.*, 9, 362 (1870). (c) Schindler, *Mag. Pharm.*, 31, 33 (1830). (d) Potilitzin, *Ber.*, 12, 695 (1879).

In the course of studying certain properties of lithium iodide, it was observed that when heated in air it evolved large quantities of iodine and that the aqueous solution of the residue not only gave an alkaline reaction but showed powerful oxidizing action, as indicated by its copious liberation of iodine from an acid solution of potassium iodide. Qualitatively, this behavior is identical with that of potassium chloride, bromide and iodide as recorded by the investigators named above, but because of the greater degree to which the reaction takes place in the case of lithium iodide, the phenomenon seemed to justify more detailed investigation.

### Experimental Part

The trihydrate of lithium iodide was dehydrated by heating in a current of electrolytic hydrogen from which traces of oxygen had been removed by passing over heated palladized asbestos, the water formed being removed by concd. sulfuric acid and phosphorus pentoxide. The dehydration of lithium iodide and the subsequent oxidation of the anhydrous salt was accomplished in a duplicate of the apparatus used by Baxter,<sup>3</sup> and by Richards and Parker<sup>4</sup> for the preparation of anhydrous hygroscopic salts. The lithium iodide was prepared in the form of the trihydrate by the method used by Baxter.<sup>3</sup> The trihydrate was dehydrated and upon analysis by precipitation of the iodine as silver iodide gave a purity of 99.89, 99.94 and 99.96%.

Qualitative examination of the residue obtained by heating anhydrous lithium iodide in an atmosphere of oxygen showed the presence of lithium oxide and lithium iodate, the latter in considerable quantity. Examination of the residue for periodates of lithium gave negative results.

Quantitative determinations of the iodine liberated and the oxide and iodate present in the residue gave results contained in Table I.

Iodine evolved, %	Iodate in residue, %	Oxide in residue, %
79.24	...	...
81.51	...	...
80.11	...	...
...	72.02	...
79.26	...	...
79.89	73.87	21.25
78.91	...	...
81.43	70.88	27.17
81.44	68.24	23.50
Av. 80.22	Av. 71.25	Av. 23.97

<sup>3</sup> Baxter, *Am. Chem. J.*, 31, 558 (1904).

<sup>4</sup> Richards and Parker, *Proc. Am. Acad. Arts Sci.*, 32, 59 (1896-1897).

### Discussion of Results

The agreement of the determinations of the amount of iodine liberated is more satisfactory than for the iodate and oxide formed in the residue. In the case of the iodate formed, the poorer agreement may be due to local overheating resulting in decomposition of the iodate into iodide and oxygen. We have no reliable information regarding the temperature at which lithium iodate begins to decompose. Lithium oxide is known to attack platinum and it is possible that this may account for the discrepancies in the determinations of the oxide. The striking feature is the large amount of iodate formed.

The equation  $10\text{LiI} + 5\text{O}_2 \longrightarrow 2\text{LiIO}_3 + 4\text{Li}_2\text{O} + 4\text{I}_2$  seems to fit the facts most closely.

	Iodine liberated, %	Iodate in residue, %	Oxide in residue, %
According to equation	80.00	75.10	24.90
Found	80.22	71.25	23.97

### Summary

1. Heating anhydrous lithium iodide in a current of pure, dry oxygen to an elevated temperature results in an evolution of iodine and the formation of lithium iodate and oxide in the residue.

2. The reaction conforms closely to the equation  $10\text{LiI} + 5\text{O}_2 \longrightarrow 2\text{LiIO}_3 + 4\text{Li}_2\text{O} + 4\text{I}_2$ .

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## THE DECOMPOSITION AND OXIDATION OF DITHIONIC ACID

BY DON M. YOST AND RICHARD POMEROY

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### Introduction

The solutions of dithionic acid ( $\text{H}_2\text{S}_2\text{O}_6$ ) and its salts are known<sup>1</sup> to be relatively unreactive towards strong oxidizing agents such as permanganate, dichromate, hypochlorous acid and bromine at ordinary temperatures. This is shown both by direct experiment and by the fact that dithionates are formed along with sulfates when the first two of these oxidizing agents react with sulfites. The only investigation that has been made is that of Muller,<sup>2</sup> who showed that iodine does not react directly with dithionic acid, but that the first step consists in the decomposition of the acid into sulfurous and sulfuric acid, and that this is followed by the reaction between iodine and sulfurous acid. The equations are

<sup>1</sup> Gmelin-Kraut, "Handbuch der anorganischen Chemie," Carl Winter, Heidelberg, 1907, vol. 1<sup>1</sup>, p. 593.

<sup>2</sup> Muller, *Bull. soc. chim.*, 9, 183, 185 (1911).