THE SPECIFIC ABSORPTION OF REAGENTS FOR GAS ANALYSIS

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A knowledge of the absorbing power of the reagents that are commonly used in gas analysis for the gases absorbed by them and for the conditions under which they are ordinarily employed would be of considerable value to the gas analyst. Definite information of this nature is for the most part lacking. Hempel¹ has proposed the term "analytical absorbing power," a suitable expression for this property, but his method of determining it seems open to objection. According to his method, an excess of pure gas was placed in contact with 1 cc. of reagent over mercury and shaken with the reagent as long "als noch schnelle Absorption erfolgte, so dass in Laufe einer Minute mindestens mehrere Kubikzentimeter verschwanden." The decrease in volume thus obtained was divided by four and this value termed the analytical absorbing power. No attempt was made to determine the absolute absorbing power of the reagent, nor was the reagent required to remove the gas completely as it must in actual service. The rapidity with which a reagent absorbs a pure gas that is present in excess is quite different from that with which it completely removes the gas from its mixture with other gases. In the first case, the pressure that is exerted by the gas is presumably that of the atmosphere, while in the second case, the partial pressure of the gas becomes less and less until it equals zero or is so small as to be negligible for technical purposes. In general, as the pressure becomes less, the rapidity of the absorption decreases, the last traces of the gas being absorbed with difficulty, or not at all. It is evident, therefore, that the values that are obtained by Hempel's method have little bearing upon the efficiency of the various reagents for quantitative absorptions, and that they afford the analyst no certainty that his reagents may be used until they have absorbed the quantity of gas indicated by the analytical absorbing power now assigned to them without possibility of the incomplete removal of the constituents.

The determination of the volume of a gas which a certain reagent will absorb up to the point at which the gas is not completely removed from its mixture with other gases is needed by gas analysts. It is here proposed to express this value in cc. of gas per cc. of reagent and term it the *specific absorbing power*, or the *specific absorption*, of the reagent. The statement of the specific absorption of a reagent for a gas must contain the name of the apparatus that is employed, the method of its manipulation, and the temperature of the reagent, since these conditions affect the results. Also the volume of gas that is absorbed at a time may have an effect upon the specific absorption and for this reason the mixture to be employed in the determination of this value should contain an amount of the gas to be removed such as would most frequently be met with, and this amount should be given in stating the specific absorption of a reagent.

¹ "Gasanalytische Methoden," 4th Ed., p. 128.

For example, the specific absorption at room temperature of a certain solution of alkaline pyrogallol for oxygen, obtained by shaking a mixture of gases containing 21 per cent oxygen with the reagent for 3 minutes in the Hempel double pipette, was found to be 5. By this is meant that successive samples of a gas mixture of the above composition were analyzed for oxygen by pyrogallol in the manner above indicated until the reagent was no longer capable of removing all of the oxygen in the time allotted. The total amount of oxygen absorbed up to that point was found to be 5 times the volume of the reagent that was employed.

Determinations of specific absorption are being made in this laboratory in connection with investigations on the most desirable concentrations of the various reagents and the most desirable conditions for their use. The results on alkaline pyrogallol are given in the following article.

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REAGENTS FOR USE IN GAS ANALYSIS

I. ALKALINE PYROGALLOL

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HISTORICAL RÉSUMÉ AND INTRODUCTION

To Döbereiner¹ is attributed the discovery of the absorption of oxygen by an alkaline solution of pyrogallol. Liebig² was the first to utilize this reaction for the quantitative removal of oxygen from its mixture with other gases. He employed a solution of potassium hydroxide of 1.4 specific gravity and added to it one-half its volume of a solution of pyrogallol containing 1 g. to 5-6 cc. of water. Much later Weyl and Zeitler³ studied the effect upon the absorbing power of the reagent of varying the concentration of the alkali. In their work, a definite volume of air was aspirated through a U-tube that contained broken glass and a measured volume of the alkaline solution of pyrogallol. The amount of oxygen that remained in the air after this treatment was determined by titration with a solution of sodium hyposulfite, using indigo as the indicator. Three solutions of potassium hydroxide, of specific gravities 1.025, 1.050 and 1.500, were employed, and the reagent was prepared by adding 0.25 g. of pyrogallol to 10 cc. of one of these solutions. The oxygen that was not absorbed under the arbitrary conditions of the experiments amounted to 1.56, 0.88 and 2.9 per cent for the solutions in which the specific gravity of the alkali was 1.025, 1.050 and 1.500, respectively. From these data the authors conclude that the solution of potassium hydroxide of specific gravity 1.050 gives the reagent with the highest absorbing power and they state also that the pyrogallol probably is quickly destroyed by the solution of potassium hydroxide of specific gravity 1.5. Wehl and Goth⁴ performed similar experiments substituting sodium

¹ Gilbert's Ann., 74 (1823), 410.² Liebig's Ann., 77 (1851), 107.³ Ibid., 205 (1880), 255.⁴ Ber., 14 (1881), 2659.