

### Summary.

It was found that by employing weight burets with appropriate precautions, six titrations of pure arsenious oxide against pure iodine gave highly precise results, the average of which agreed within 1 part in 3600 with the theoretical value. The evidence is in favor of arsenious oxide as the more reliable standard substance in practice. Precautions in the preparation and use of standard iodine solutions are emphasized.

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### NOTES.

**Retardation by Sugars of Diffusion of Acids in Gels.**—In a paper under this title, E. A. and H. T. Graham<sup>1</sup> have occasion to refer to the power of salt and of sugar to decrease the swelling of gelatin which has been immersed in dilute acid solution and has become swollen in consequence. They state that "the decrease of swelling by sugar cannot be accounted for by Procter's ion concentration theory, but must be explained in some other way." Procter attributes the swelling of gelatin in acid solution to the fact that the anion of a highly ionizable salt formed from the acid and gelatin tends to diffuse outward, and the amount of swelling to the excess of concentration of diffusible ions in the jelly over that in the external solution. In the case of an equilibrium between a colloid jelly and a solution of electrolytes, at least one of which forms an ionizable compound with the colloid, it has been shown<sup>2</sup> that the concentration of diffusible ions in the jelly must always be greater than in the surrounding solution; likewise that adding to such a system an electrolyte which does not interact chemically with any of the components of the system must result in a lessening of the excess of concentration of ions in the jelly over that in the external solution and therefore in a reduction of the swelling. This explains the action of salt.

Procter and Wilson, however, dealt only with highly ionized electrolytes and assumed that the very small concentration of neutral molecules was the same in both phases. The quantitative agreement between their theoretical calculations and experimental data shows that no serious error was introduced by this assumption. But, where a mixture of electrolyte and non-electrolyte is concerned, it is necessary to take into consideration the effect of thermodynamic environment. Since the molal fugacity of neutral molecules increases very rapidly with increasing concentration of ions in a solution, the molal fugacity of sugar would be greater in the jelly than in the surrounding solution and hence, upon the establishment of equilibrium, the sugar will have become

<sup>1</sup> THIS JOURNAL, 40, 1916 (1918).

<sup>2</sup> Procter and Wilson, *J. Chem. Soc.*, 109, 307 (1916); J. A. and W. H. Wilson, THIS JOURNAL, 40, 886 (1918).

more concentrated in the external solution than in the jelly. If this lessening of the excess of concentration of diffusible ion and molecular species in the jelly over that in the external solution results in a corresponding lessening of the difference between the total diffusion pressures of the two phases, then diminution of the volume of the jelly is a necessary concomitant. So long as we are ignorant of the quantitative relations connecting the reciprocal alterations of molal fugacities of neutral molecules and ions in the presence of each other, it must be admitted that Procter's theory is capable of giving at least a plausible explanation of the power of sugar to decrease the swelling of gelatin.

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**The Permanent Marking of Glass Vessels.**—It is very often desirable and frequently necessary for the chemist to mark glass vessels permanently. This is usually done by means of a diamond or hydrofluoric acid. While the latter procedure gives good results if done carefully, it is a rather troublesome and lengthy process. The use of the diamond requires considerable practice in order to produce good markings, besides it is not always advisable to use it. A preparation called Diamond Ink, usually a mixture of ammonium fluoride, hydrofluoric acid and barium sulfate, produces permanent marks and is easily applied. It is, however, difficult to obtain sharply defined markings with this method; furthermore the writing is not clearly visible if the surface becomes wet.

The present note proposes the use of glass color fused in the glass by means of an ordinary burner. In glass painting, the glass colors, mostly mixtures of low fusing silicates and metallic oxides, are mixed with some vehicle and applied to the glass. They are then "fired" in a kiln at a temperature not exceeding 590° C. (Seeger Cone 022). This procedure is, of course, not applicable as such to ordinary laboratory conditions.

As the "firing" in the present method is done by means of a burner, many of the glass colors could not be used, because they undergo chemical changes when exposed to the flame.

In order to apply the colors<sup>1</sup> they are intimately mixed with a vehicle (made up of 4 parts copaiba balsam, 1 part clove oil, 1 part lavender oil). The colors which have been found most suitable are: Green 728D,<sup>2</sup>

<sup>1</sup> The colors used are obtainable from the Roessler & Hasslacher Chem. Co., Ceramic Dept., Perth Amboy, N. J. (N. Y. Office, 100 Williams Street). The oil can undoubtedly also be obtained there. Many stores handling colors for china painting will have these materials on hand.

<sup>2</sup> Numbers refer to Roessler & Hasslacher products.

Blue 1079D and a mixture of Brown 695D and White Enamel 1310D. The Brown alone can only be used on hard glass or porcelain where higher temperatures can be applied.

The actual procedure is herewith described: The glass color (use Green 728D) in powdered form is mixed<sup>1</sup> with just enough of the oil, so it will still run from a pen. A so-called crow-quill (steel) pen is recommended, a fine brush is also very good, but more difficult to handle. The desired markings are made on the clean glass surface. The marked article is then warmed evenly over a flame to dry the oil and also to prevent cracking in the final heating. The place where the marking has been made is now heated by holding against the *side* of the flame of a burner,<sup>2</sup> the flame touching the marking on a tangent, the article being rotated part of a circle. During this heating the mark is watched carefully. The color will first turn black through the carbonization of the oils, then it will begin to glow a dull red. At this point the article is removed, allowed to cool a little and reheated until the markings, not the glass, again begin to glow.

The marking so obtained presents a smooth, shiny surface. It cannot be removed by mechanical or the usual chemical means. We consider the marking successful, when it cannot be removed mechanically (scratching or scouring), after a twenty-four-hour immersion in "cleaning mixture."

The paint should be mixed as thick as practicable. The heating must be done carefully to avoid caving in or other distortions of the vessel. If porcelain crucibles are to be marked, the color is applied as indicated above, the vessel is then heated in the usual way on a triangle over a free flame.

It may be of interest to mention some of the uses to which this procedure has been put. We have graduated test-tubes for special work p. e. for Benedict's colorimetric sugar method (12.5 cc. and 25 cc.) or graduated test-tubes to replace small graduated cylinders. Pipets were graduated in the laboratory. Kjeldahl flasks may be marked to indicate the maximum volume to which they may be filled (students use). Beakers were graduated in 50 cc. or 100 cc. intervals. It is also advantageous to graduate distilling flasks roughly, to know the approximate liquid contents in the course of evaporation. The proposed procedure is especially valuable in the last mentioned instances, because any deep etching or engraving weakens the vessel.

The most difficult problem is the marking of microscope slides. Their

<sup>1</sup> Mixing can be done on a glass plate with a small spatula. Where a small amount of work is contemplated the indentations of an indicator tile have been found useful.

<sup>2</sup> A Méker burner has been found best. The article should best be held near the base of the flame.

heating requires great care and considerable experience in order to avoid an undue amount of breakage. They must be heated *over*, not on the side of a burner, the marked side toward the flame. It is our opinion that a muffle should be used where a large amount of slides are to be marked, using a strip of zinc (m. p.  $412^{\circ}$  C.) and a Seger cone 022, to indicate the temperature limits. Since a muffle furnace was not available, we were unable to carry out this experiment. The marked slides, after being thoroughly dried, may be sent to some shop where glass firing is done and finished there for a nominal charge.<sup>1</sup> JOSEPH C. BOCK.

[CONTRIBUTION FROM THE WISCONSIN PHARMACEUTICAL EXPERIMENT STATION.]

### OPTICALLY ACTIVE PINENE NITROSOCHLORIDE AND SYNTHETICAL ACTIVE PINENE.

BY E. V. LYNN.

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The nitroso compounds, characterized by the group  $\text{—N} = \text{O}$ , were first prepared by Cahours,<sup>2</sup> in 1842. The discovery by Tilden,<sup>3</sup> in 1875, that they could be prepared by addition to unsaturated compounds, and the subsequent improvement in the method by Wallach,<sup>4</sup> in 1888, first placed these nitroso compounds in the important position they have since occupied.

Although a blue coloration generally accompanies the commencement of the reaction, the compounds which result are, in most instances, colorless. The latter have been shown to be isonitroso compounds,<sup>5</sup> characterized by the group  $\text{=N—OH}$ , or bisnitroso compounds,<sup>6</sup>  $\text{R}'\text{—N}_2\text{O}_2\text{—R}'$ . Since the blue substances which have been isolated<sup>7</sup> are shown to be true nitroso in character, and since they readily change to the isomers<sup>8</sup>

<sup>1</sup> A semi-permanent marking medium can be obtained by mixing a pigment (lead oxid, lampblack, etc.) with a good spar varnish, canada balsam or collodion varnish (banana liquid). It will resist the ordinary cleaning and has been found useful for marking stock bottles and similar containers.

<sup>2</sup> *Ann.*, **41**, 76-77 (1842).

<sup>3</sup> *J. Chem. Soc.*, [2] **13**, 514-518 (1875); *Ibid.*, **31**, 554-561 (1877); *Pharm. J.*, [III] **8**, 188-191 (1878).

<sup>4</sup> *Ann.*, **241**, 241-254 (1888); **253**, 249-267 (1889).

<sup>5</sup> Goldschmidt, *Ber.*, **18**, 1729 and 2220 (1885); Kremers and Urban, *Am. Chem. J.*, **16**, 395-404 (1894); Meyer, *Ber.*, **21**, 1291-1295 (1888); Kremers and Mead, *Am. Chem. J.*, **17**, 607-611 (1895).

<sup>6</sup> Kremers, *Inaug. Diss.*, Göttingen, 1890; Baeyer, *Ber.*, **28**, 639-652 (1895).

<sup>7</sup> Wallach, *Ann.*, **241**, 312 (1887); Baeyer, *Ber.*, **27**, 436-454 (1894); Thiele, *Ibid.*, **27**, 454-456 (1894); Chapman, *J. Chem. Soc.*, **67**, 780-784 (1895); Piloty, *Ber.*, **31**, 218-220 (1898); Kremers and Schreiner, *Pharm. Arch.*, **2**, 273-300 (1899); Schmidt, *Ber.*, **35**, 3373 and 3727 (1902); Piloty and Steinbock, *Ibid.*, **35**, 3101-3117 (1902); Schmidt, *Ibid.*, **36**, 1765-1768 (1903).

<sup>8</sup> Kremers and Schreiner, *Pharm. Arch.*, **2**, 273-300 (1899).