pearance of a faint but distinctly perceptible pink color. An additional two drops of the thiocyanate solution should make the color quite strong and prove that the true end point had been attained.

The Handling of Liquid Substances.—In analyzing liquids we used a glass tube 30 mm. long and 6 mm. in internal diameter, one end of the tube being sealed with a thickness of 3–4 mm. of paraffin wax. During the weighing, the tubelet was closed with a cork, which was removed immediately before tubelet and substance were introduced into the alcohol in the Kjeldahl flask.

A Qualitative Test for Halogen.

Our uniform success with the method described above suggested its use also as a qualitative test for halogens in organic compounds. A series of trials, using *p*-chlorobenzoic acid, *o*-chlorophenol, bromobenzene, bromonaphthalene, and iodoform, showed that the merest traces of halogen can be positively detected by the following simple procedure:

A few milligrams of the given substance are dissolved in one cubic centimeter of pure absolute alcohol; a few small bright pieces of pure metallic sodium are thrown into the solution, one at a time, with gentle warming toward the end; on cooling, the solution is acidified with 1 cc. of dilute nitric acid (3 parts of water to 1 part of acid), and filtered, if necessary; after testing the acidity of the solution, 10 drops of an approximately $N/15$ silver nitrate solution are added. A parallel blank test will of course make the result surer.

In this way, for instance, we plainly detected chlorine in 1 drop of a liquid produced by adding a single drop of carbon tetrachloride to 30 cc. of benzene. In the same case the Beilstein test gave a doubtful result.

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A POSSIBLE SOURCE OF ERROR IN COLORIMETER OBSERVATIONS.

BY J. H. LONG.

Received December 27, 1915.

Something over a year ago, in a series of observations just started, and in which a Duboscq colorimeter was employed, I noticed a marked variation from an anticipated result. The instrument had been in use for years and had always shown a correct zero point when the bottom of the glass cell and the plunger prism were brought in contact.

The standard colored liquid was in the left-hand cell and the one under investigation in the right. The observed column lengths were about 80 and 100. (The exact values are not recalled, but these are given to illustrate the situation.) The concentration of the investigated liquid was therefore about 80% of the other. On reversing the liquids, that is, putting the standard in the right-hand cell and adjusting the plunger to

80 divisions the reading on the left was found to be about 91 divisions. This made the apparent strength of the unknown about 88% of the standard strength.

This discrepancy suggested that the actual lengths of the liquid columns must be different from those read off, which would be the case if the plungers had dropped from their normal positions. A control of the zero point showed this to be the fact; one plunger had dropped about three millimeters, and the other five, or six and ten divisions, respectively. The column lengths first observed were then actually 74 and 90, giving 82, in place of 80% strength as the relation of the liquid to the standard.

After the reversal of the two liquids we have actually on the right side 70 divisions, against 85 on the left, as the real length of the liquid columns, which gives the correct relation. The sinking of the prism plungers had shortened the two columns in unequal degrees, giving rise to rather large errors. The prisms seem to be fastened in their brass sockets by means of a wax which is too soft for the purpose and which softens enough in our summer climate to allow the prisms to drop down a little. The situation described here was noticed after the instrument had stood through a hot summer vacation in a room facing the south and west, the temperature in which often reached 33°. Experiment showed that at this temperature the wax became appreciably softer, and soft enough to permit the slow displacement of the glass. I have since noticed the same defect in other instruments of the same type. Even greater errors are possible where the instrument is allowed to stand near a radiator or in a room where the temperature is always too high from overheating by steam. The prisms may even drop from their sockets in instruments left in this way.

If both prisms should drop to the same extent the error might be smaller but would not disappear. Assume, for example, that with the standard liquid in one cell the prism is set to give a depth of 10 millimeters in the column below. Or, in the form of instrument in which the cell and not the prism is moved, the former is brought up to make this apparent length of liquid column. In the other cell a depth of 12 millimeters is necessary to give the same shade. The concentrations of the liquids would then appear to be related as 12 to 10. If both prisms had dropped to the same degree, say 3 millimeters each, the actual lengths of the liquid columns would be, not 10 and 12, but 7 and 9. The relation of these lengths is no longer the same. Great errors are possible where short liquid columns are employed, and with unequal displacement of the prisms the weaker liquid may actually appear the stronger. For example, with an apparent depth of column in the standard cell of 10 millimeters, or divisions, the color equality in the other cell is reached with a depth of 8 millimeters, or divisions, of the scale. The strength of the unknown

liquid would then appear to be five-fourths of that of the standard. But if the prism in the standard cell had dropped 5 divisions, and the other only 2, for example, the actual lengths of columns of liquid would be 5 and 6 divisions, respectively, with the unknown having then a strength five-sixths of that of the other

In the well-known creatinine estimation, where relatively long columns are employed, such large errors are not possible, but in many other comparisons, with short columns, they doubtless actually occur. It is therefore desirable to control the zero point frequently by bringing the end of the prism in contact with the bottom of the cell and noting that the reading is at the end or zero of the scale. Care should be taken to keep the instrument away from the vicinity of steam radiators, and, in general, in a place where the temperature does not become high in summer.

Others may have had similar experiences with the Duboscq instrument, but as I have not seen them discussed in print I think it worth while to call attention to the facts in this way.

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CHEMICAL CHANGES OCCURRING DURING THE RIPENING OF THE WILD GOOSE PLUM.[1]

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Received January 17, 1916.

The beginning of the study of chemical changes that take place during the ripening of fruits dates back to the time of the phlogiston theory. Sennebier,[2] after experimenting on a variety of fruits, supposed that they suffered a loss of phlogiston during the ripening process.

De Saussure,[3] about 1820, carried on researches on the ripening of fruits and as a result of his investigations advanced the theory that fruits act like leaves in their respiratory functions. The fallacy of his theory was later shown by Berard,[4] who carried on respiration experiments on fruits in vessels containing hydrogen, nitrogen, carbon dioxide, and *in vacuo*. In all cases he found an increase of carbon dioxide at the expense of the oxygen, and in no case the reverse change. Similar experiments were tried on fruits still attached to the tree, with the result that the fruit did not mature, but became withered and browned, showing that oxygen is necessary for the ripening of fruits. Apparently the work

[1] Read before the Lexington Section of the American Chemical Society, January 13, 1916.

[2] *J. pharm. chim.*, [2] **7**, 249 (1821).

[3] "Recherches Chemiques sur la vegetation," Paris, 1840.

[4] *Ann. chim. phys.*, [2] **16**, 152, 225 (1821).