

8. **Fletcherism** of starchy foods should be encouraged so as to insure the salivary digestion of a large quantity of material.

9. The results of the present experiment so far as protein utilization is concerned do not support the claims of Horace Fletcher and his followers for the efficiency of excessive mastication of food, nor do they demonstrate the harmfulness of food-bolting to the organism.

PHILADELPHIA, PA.

### NOTES.

**A Convenient Apparatus for Chlorination with Phosphorus Pentachloride.**—The common methods employed in chlorinating solid organic compounds, such as the sulfonic acids or their metallic salts are: (1) Shake material and  $\text{PCl}_5$  together in a flask with or without reflux condenser, some authors advocating the use of a one-hole stopper and tube for the delivery of the  $\text{HCl}$  gas just above the surface of water in a bottle or flask. (2) Grinding material and  $\text{PCl}_5$  together in a mortar or evaporating dish.

In method (1) it is difficult to thoroughly mix the materials, and the reaction is often slow in starting. In (1) and especially in (2) the large amounts of  $\text{HCl}$  gas evolved make the use of a hood necessary and the operation unpleasant at best. In this laboratory it has been customary to perform (2) out of doors.

The authors while working on sulfonic acid derivatives devised the following simple apparatus:

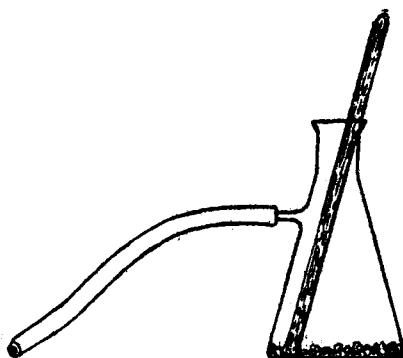
The material is placed in a heavy-walled, side-neck filter flask attached to a Richards or similar filter pump. Suction is applied and the  $\text{PCl}_5$  added. The materials are ground together with a pestle made from heavy glass rod or large tubing. No  $\text{HCl}$  fumes escape into the air, making the use of a hood unnecessary.

If but small amounts of material are available a thick-walled, side-neck test tube may be used.

The method is, of course, not applicable if the product of chlorination is volatile.

STUART P. MILLER AND FRANKLIN C. GURLEY.

LABORATORY OF ORGANIC CHEMISTRY,  
MASSACHUSETTS AGRICULTURAL COLLEGE,  
March 1, 1915.



TO PUMP

**The Condensation of Vanillin and Piperonal with Certain Aromatic Amines.**—In a private communication J. R. Furlong calls my attention to the fact that some of the condensation products described under the above title (THIS JOURNAL, 35, 976 (1913)) were previously described by Manchot and Furlong (*Ber.*, 42, 4387). The compounds referred to are products of condensation of vanillin with *p*-aminobenzoic acid and with its ethyl ester and of piperonal with *p*-aminobenzoic acid.

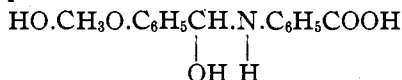
There are a number of points, however, in which our observations and conclusions are at variance and I take this opportunity to mention them.

Manchot and Furlong condensed vanillin and *p*-aminobenzoic acid in boiling alcohol, obtaining a product which was "not crystalline" and "could not be crystallized in any way." They further state that if toluene is used as solvent in the preparation that "no reaction takes place." These statements are in striking contrast to my observations, in view of the fact that I use toluene as a solvent, with or without 5% of alcohol, and obtain a very beautiful crystalline product, melting at 211–2° instead of 209°, as given by Manchot and Furlong. The crystals, if formed slowly, are compact and brilliant; if formed quickly, are thin plates with sharply bevelled ends. Single crystals under the microscope appear colorless but in the mass are bright yellow. The reaction in toluene is indeed slow and the results obtained after boiling a few minutes might lead one astray. The reaction has begun, however, and is complete after boiling ten hours. Again Manchot and Furlong state that when heated with toluene, alcohol or benzene the compound breaks up, and yet I depend upon toluene for its preparation and its purification. In a special test on this point a small amount of the pure substance was dissolved in boiling toluene and cooled down. The crystals which separated had the same melting point as before. The filtrate was evaporated to dryness and only a trace of material was left. The toluene had been dried with calcium chloride. Alcohol, which Manchot and Furlong used, converts much of the compound into a varnish, even when allowed to evaporate spontaneously.

The red compound obtained by boiling the above compound in water is also in dispute. Manchot and Furlong state that it loses color at 75–7° and melts at 190–200°. I stated that it melts at 104–6° and might have added that it loses color as it re-solidifies with rising temperature and melts again at 190–200°. The behavior of the product when heated is, in fact, very irregular. Melting points from 84° to 106° may be obtained, depending upon the rate of heating or upon the temperature of the bath when the substance is placed in it. It is also an incomplete statement to say that it loses color at 75–7° because it loses color over a wide range of temperature, even as low as 65°. The formation of the red

compound is very rapid, the same product being obtained whether the anil is boiled 5 minutes with water or one hour.

Manchot and Furlong state that in the formation of the red compound the anil has taken up water as H and OH at the double bond, thus:



I had concluded that it was water of crystallization, but Furlong objects to this explanation, saying that I offer no evidence in support of it. I reply that it seemed the natural explanation. One thinks at once of such compounds as oxalic acid which melt in their water of crystallization, lose their water and then melt again at a much higher temperature. Other compounds like copper sulfate lose their color when the water is driven off. In the case of the red products, single crystals are reddish yellow but upon losing water they are quite colorless under the microscope. Manchot and Furlong's explanation, as they say, is that assumed by Hantzsch and Schwab (*Ber.*, 34, 829), who state that benzylidene-*p*-chloraniline hydrochloride takes up a molecule of water. This is however under the influence of a soda solution cooled below 0°. And further it is to be noted the benzylidene compound has already taken up a molecule of hydrochloric acid at the nitrogen atom. The case then is not analogous. Further, according to this explanation, an unsaturated compound becomes saturated and assumes its unsaturated character just as easily. The formation of the red compound undoubtedly begins at 70°, for Manchot and Furlong obtained a red oil in water at that temperature. I find that the water can be driven out of the compound at the same or even at a lower temperature. If the modern theory is true that unsaturated compounds are in a state of strain, involving a greater difficulty in producing unsaturated compounds than in producing saturated, this reversibility should not occur.

Furlong also refers to the lower melting point, 233-4°, which I gave to the condensation product of piperonal and *p*-aminobenzoic acid, whereas he found 242°. In view of the secondary product, melting at 171-3°, obtained when toluene is the solvent, whereas the use of alcohol seems to yield no such product, the figure may be too low, although the analysis does not indicate so great a difference.

Furlong finally refers to my hope of finding isomeric compounds in this field and states that Manchot and Furlong found that the condensation product of ethyl *p*-aminobenzoate and salicylic aldehyde occurs in two forms. At a later date Manchot and Palmberg (*Ann.*, 388, 103) regarded this as a case of keto-enol isomerism but were unable to obtain any ketone derivatives such as oximes to establish their conclusion. This view was based solely on the observation that ferric chloride acts more quickly

on one form than on the other at temperatures obtained by a mixture of carbon dioxide and acetone. This leaves much to be desired in the way of characterizing the keto form.

ALVIN S. WHEELER.

UNIVERSITY OF NORTH CAROLINA.

### NEW BOOKS.

**The Chemistry of the Radio-Elements.** Part II. By FREDERICK SODDY. Longmans, Green & Company. 44 pp. Price, \$1.75.

The second part of Soddy's well-known book deals with the radio-elements and the periodic law. In the first chapter he brings the several theories discussed in Part I, up to date, and then goes into a somewhat detailed discussion of the work of A. S. Russell, K. Fajans and A. Fleck on isotopes or the chemically nonseparable elements. It is shown that when an  $\alpha$ -particle is expelled it carries with it two atomic charges of positive electricity, and the expulsion of these two positive charges from the atom affects the valency of the product exactly as in ordinary electrochemical changes of valency. In the case of  $\beta$ -particle, which is a negative electron, the loss of this single atomic charge of negative electricity increases the positive valency of the product by one. In other words, the expulsion of an  $\alpha$ -particle causes the element to shift its position in the periodic table by two places in the direction of diminishing mass so that the product is in the family next but one; the loss of a  $\beta$ -particle, however, causes the element to shift its position in the periodic table by one place in the opposite direction to that for an  $\alpha$ -ray change. A loss of one  $\alpha$ - and two  $\beta$ -particles, therefore, brings the product back into the same family as the parent. These elements are found to be nonseparable chemically, and are called *isotopes*. In general terms, "whenever two or more radio-elements fall into the same place in the periodic table, then independently of all considerations as to the atomic mass, the nature of the parent element and the sequence of changes in which they result, the elements in question are chemically nonseparable and identical." It is shown that this identity probably extends to the spectrum reactions and all physical properties with the exception of mass.

The final products of the disintegration of the thorium and uranium series fall in Group IV, Family B, and have atomic weights very close to that of lead. These elements are, therefore isotopes and are chemically nonseparable. In addition, they are isotopic with Radium B, Thorium B, Actinium B and Radium D. The possibility, therefore, of lead being a mixture of two or more chemically nonseparable elements is a pertinent one. T. W. Richards and Max Lambert have recently determined the atomic weight of lead obtained from radioactive minerals, and find the atomic weight to vary from 206.40 to 206.86, a very considerable variation from the atomic weight of ordinary lead, *viz.*, 207.15. Soddy, working