

dish, the ligroin is removed, the vanillin is dried at not above 55° C. and weighed. This gives a pure crystalline product, melting at 80°–81° C. After the weighing, a melting-point determination should be made, and then color tests may be applied. Some samples of vanilla extracts have been found to contain phenol-like bodies resembling creosol in odor and chemical behavior. These give color compounds with salts of iron; hence, any volumetric estimation, or even qualitative test, applied to the unpurified extract may be fallacious when based on color reactions of iron salts.

Results were obtained by this method under control as follows: From Mexican vanilla beans, a liquid product was made by following the directions of the United States Pharmacopoeia. Of this tincture, twenty-five grams were taken in duplicate portions; to each was added five-tenths gram of pure crystallized coumarin, and the analysis was made for estimation of coumarin and of vanillin. The coumarin recovered from the duplicate portions was, respectively, 0.491 gram or 98.2 per cent. of that taken, and 0.482 gram or 96.4 per cent. of that taken. The vanillin recovered was, respectively, 0.3081 gram and 0.2997 gram, from each of the portions of twenty-five grams of the tincture.

This method for vanillin is much easier and quicker to work than the sodium bisulphite method, and has these advantages: (1) the shaking out with ammonia water is quickly done; (2) the alkaline solution of vanillin thus obtained is small in bulk; (3) the trouble of getting rid of sulphur dioxide is avoided. The separation of the vanillin is also more complete.

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### NEW METHOD FOR THE PREPARATION OF CESIUM.<sup>1</sup>

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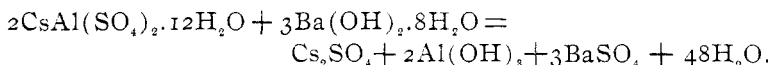
WINKLER<sup>2</sup> tried to reduce cesium carbonate with metallic magnesium, in both glass and porcelain tubes in a current of hydrogen. He, however, obtained no cesium. Beketoff<sup>3</sup> states that it can be obtained in small quantities by the electrolytic reduction of the cyanide; he also acted on the hydrate with aluminum, but the yield was poor. In 1894 he

<sup>1</sup> Read by title before the New York meeting of the American Chemical Society, December 28, 1898.

<sup>2</sup> *Ber. d. chem. Ges.*, 23, 53.

<sup>3</sup> *Bull. Acad. Petersburg*, 4, 247.

made a small amount by acting on cesium alum with metallic magnesium.<sup>1</sup> We made a great many experiments with a view to improving these processes, but finally found that a different method worked remarkably well, and if the directions are exactly followed it is absolutely free from danger. We found that by heating cesium hydroxide with magnesium powder in a red-hot tube through which passed a current of hydrogen, we could obtain nearly the theoretical amount of cesium. Inasmuch as we always commenced with cesium alum, and as that is the cheapest and most available salt to begin with, we will give all the details of the method that we finally found to be the best. The cesium alum should be first converted into cesium sulphate. It is not advisable to convert it directly into cesium hydroxide on account of the fact that too much water is required to dissolve the cesium alum, and also because cesium hydroxide absorbs carbon dioxide very rapidly. In order to convert cesium alum into cesium sulphate the following reaction can be used:



Dissolve the cesium alum in as small a quantity of boiling-water as possible (it is more convenient in all operations connected with cesium to use casseroles rather than dishes or beakers), and in a separate casserole dissolve the crystalline barium hydroxide; when both are in solution, mix the two and filter rapidly with a good pump; a Buchner funnel can be used in this operation to great advantage. The filtrate if slightly alkaline, due to an excess of barium hydroxide, should be treated with carbon dioxide for a few minutes and quickly refiltered. It can now be either evaporated to dryness or crystallized. The next step is to convert the cesium sulphate into cesium hydroxide.



The sulphate is quite soluble in hot water, and as small a quantity of the solvent as possible should be used. The barium hydroxide should also be separately dissolved in a very small quantity of water. When both are in solution mix and filter with a suction-pump and Buchner funnel. The filtrate is

<sup>1</sup> *Proc. Russ. Phys. Chem. Ges.*, 1894.

rapidly evaporated to dryness in a silver crucible and then fused; it should now be poured into a silver dish so that it will make a thin brittle cake of cesium hydroxide, which must not be exposed to the air longer than is absolutely necessary; it is quickly broken, transferred to a warm dry bottle, and weighed; then put into a hot porcelain mortar, broken into small pieces about half the size of a pea, and mixed with one-half its weight of magnesium powder (the magnesium powder must be previously heated in a current of hydrogen to get rid of the fat with which it is always mixed); the mixture is then quickly dropped into a clean, dry, rust-free malleable iron tube of the following dimensions: one meter long, fifteen mm. diameter, three mm. thick, and fifteen cm. from the end it is bent to an angle of about  $125^\circ$ . In order to keep the mixture in the tube a small bundle of clean piano wire irregularly twisted together is forced into the tube down the long part to the angle, before dropping in the mixture. In filling the tube it is best held inclined. The tube is now laid in a slightly inclined combustion furnace, to aid the flow of the liquid metal and quickly connected to a Kipp hydrogen generator. The hydrogen must be passed through permanganate solution in order to oxidize hydrogen arsenide and then thoroughly dried by sulphuric acid and phosphoric anhydride; the bent end of the tube is immersed in liquid paraffin to the depth of about two cm. It is advisable to have the paraffin in a casserole about seven and one-half cm. in diameter. To begin the distillation, light the burner farthest away from the mixture (the tube should never be more than one-third full), and allow hydrogen to pass through at the rate of about forty bubbles per minute. When the temperature has risen as high as one burner can produce, light the next but do not turn on full pressure immediately; this process must be continued, burner by burner, until reaction begins. This is readily marked by an increase in the speed of bubbling through the paraffin. If the bubbles come faster than 80-100 per minute, turn out the last-lighted burner and remove the tile over the tube. Bubbling will now gradually cease, due to the probable formation of hydride of cesium, decomposed at high temperatures; consequently the hydrogen pressure must be increased until gas comes through the paraffin. When

the back suction is relieved the hydrogen stream can be restored to its normal rate. This operation must be continued until all the burners are lighted and the temperature is full red. The angle piece of the tube, which should be as close to the furnace as possible, is now heated by a powerful Bunsen burner, and constantly struck with a piece of iron. The metallic cesium which has distilled into this part of the apparatus, will be liquefied, and will trickle down under the paraffin, collecting in silvery drops. The cesium comes out of the tube at the very end of the process and not before. If the foregoing directions are closely followed the whole operation can be accomplished in four hours without the slightest difficulty or danger. Explosions only occur when the tube is heated too rapidly and not sufficient attention paid to the pressure regulation. It is evident from the result of these experiments that Winkler was mistaken in stating that it is impossible to obtain cesium from its compounds by the aid of magnesium. We made cesium in quantity by our method and are now studying its physical properties.

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## THE OXIDATION OF FORMIC ALDEHYDE BY HYDROGEN PEROXIDE.<sup>1</sup>

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A FEW preliminary experiments seemed to indicate that the oxidation of formic aldehyde by hydrogen peroxide, could be easily and certainly followed by determining the quantities of formic acid produced as the result of the oxidation, by standard alkali, using phenolphthalein as the indicator. A study of this oxidation was therefore undertaken. A number of oxidations, involving hydrogen peroxide as the oxidizing agent, have been studied. The work of Magnanini<sup>2</sup> and that of Harcourt<sup>3</sup> and Essen on the effect of this substance on hydriodic acid, under different physical and chemical conditions, is important and interesting in this connection. A study of the oxidation of gaseous acetic aldehyde by oxygen gas was undertaken a short

<sup>1</sup> Read before the Boston meeting of the American Association for the Advancement of Science, August 25, 1898.

<sup>2</sup> *Gaz. chim. ital.*, 20, 377, 1890.

<sup>3</sup> *Phil. Trans.*, 1867, 157, 20, 460 and *Phil. Trans.*, 1895, 186, 817, 895.