

Still, we must not leave unmentioned the fact that the proportionality between the velocity and the square of the concentration of the silver acetate is not absolutely exact. While the change of the original concentration of the formate exerts no definite influence upon the constants of the third order, yet, as will be seen from the last table, there occurs with every diminution of the original concentration of the silver salt, a slight, but still unmistakable, increase in the values of the constants C_3 . As to the cause of this phenomenon, nothing can be said with certainty. It is not improbable, however, that the greater velocity in the more dilute solutions depends upon the greater dissociation of the silver salt, it being then assumed that only the silver ions are capable of reacting.

V. SUMMARY.

By this research it is established that the reaction between sodium formate and silver acetate proceeds with a velocity which is proportional to the concentration of the former salt, and nearly proportional to the square of the concentration of the latter. As this reaction, according to prevailing molecular ideas, takes place between one molecule of the formate (or of its anion) and two molecules of silver acetate (or of its silver ion), its observed velocity is in accordance with the theoretical requirements, and it furnishes a new confirmation of the influence of the number of the molecules taking part in reactions.

COUMARIN AND VANILLIN, THEIR SEPARATION, ESTIMATION AND IDENTIFICATION IN COM- MERCIAL FLAVORING EXTRACTS.¹

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Received November 27, 1898.

IT is a common practice in preparing an extract of vanilla from vanilla beans, to introduce also, as a lower-priced material, a portion of tonka beans. This makes a cheaper article and one that is generally popular with consumers. It is understood, however, to be an inferior article when compared with the genuine, and it can no longer be correctly labeled "Vanilla Extract." Under this name the presence of tonka extract constitutes an adulteration and hence the separation, identification, and esti-

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

mation of coumarin, the odoriferous principle of the tonka bean, has become a practical problem for the analytical chemist.

THEORY FOR THE SEPARATION OF COUMARIN FROM VANILLIN.

Vanillin is hydroxymethoxybenzoic aldehyde, while coumarin is the anhydride of coumaric (orthohydroxycinnamic) acid. The separation depends on the aldehydic character of vanillin. If vanillin be dissolved in pure dry ether and dry ammonia gas passed through the solution, the aldehyde ammonia compound of vanillin will be precipitated in almost quantitative proportions. It is accordingly not very soluble in ether; but like all aldehyde ammonias it is very soluble in water. Ammonia water should, then, extract all the vanillin from an ether solution. This theoretic principle is fully borne out in practice, as has been proved by repeated experiment. Coumarin, on the other hand, remains wholly in the ether solution.

METHOD OF ANALYSIS.

A sample of 25 to 100 grams of the commercial extract to be examined is placed in an evaporating dish, and the alcohol is allowed to evaporate at about 80° C. Water is added from time to time to keep the amount of liquid about equal to the original volume. When the alcohol is all gone, normal lead acetate solution is added drop by drop until no more precipitate forms. Stirring with a glass rod aids in the flocculation and settling of the precipitate. The solution is now filtered, best through an asbestos funnel under pressure, and the precipitate washed with a few cubic centimeters of hot water. The cooled filtrate is now extracted with ether¹ by shaking out in a separatory funnel. About fifteen to twenty cc. of ether are used each time, and the process of shaking out is repeated until a few drops of the ether evaporated on a watch glass leaves no residue. If the shaking is done thoroughly, three to four times' shaking out will usually be sufficient to extract all the vanillin and coumarin. The combined ether extracts are introduced into a second separatory funnel and shaken out with dilute ammonia (one part strong ammonia to two parts of distilled water) using about two cc. of the alkaline water solution at a time, and repeating the

¹ Chloroform may be used instead of ether here and throughout the process, with this advantage that the evaporation of the chloroform leaves the residue dryer than it is when ether is used.

process until the ammoniacal solution is no longer colored yellow. The ether solution is washed with two cc. of water and this wash-water added to the alkaline extract. The ammoniacal solution is set aside for the estimation of vanillin. The ether solution is now poured out into an evaporating dish, and the ether allowed to evaporate spontaneously, or better, the dish containing the ether is placed in a vacuum desiccator over sulphuric acid, when the ether may be removed quickly. To prevent bumping of the ether and consequent loss during distillation *in vacuo*, a capillary tube sealed at one end is so placed in the liquid that the open end projects into the centre of the solution, while the sealed end extends well out of the liquid, and rests on the side of the dish. It is necessary that the tube be long enough to prevent its resting horizontally on the bottom of the dish.¹

For Coumarin.—The residue having been left *in vacuo* over sulphuric acid long enough to remove all water, or else dried in an air-bath at not above 45° C., is treated with a few cubic centimeters of cold ligroin,² the latter being poured off into a clean dry weighed dish. The extraction with ligroin is repeated until a drop evaporated on a watch-glass leaves no residue. The ligroin is allowed to evaporate (best *in vacuo* in a desiccator containing paraffin), is dried at not above 45° C. and weighed. This gives pure crystalline coumarin, melting at 67° C. After weighing, a melting-point determination should be taken, and this, with the odor which is characteristic at this point in the analysis when compared with that of a known sample, is sufficient for its identification.

For Vanillin.—The ammoniacal solution obtained above is rendered slightly acid with ten per cent. hydrochloric acid. It is then shaken out with ether in the manner stated before. The ether is removed and the residue is dried *in vacuo* over sulphuric acid or else in an air-bath at not above 55° C. This residue is washed repeatedly with boiling ligroin, using a few cubic centimeters at a time to remove the vanillin and free it from adhering substances. The ligroin solution is decanted into a weighed

¹ Tiny capillary tubes are very useful in preventing bumping in boiling liquids, and are made by drawing out a glass tube to the dimensions of a hair. Cut the tube into a convenient length and fuse up one end.

² A petroleum fraction boiling between 30° and 40° C.

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.

UNIVERSITY OF MICHIGAN,
November 18, 1898.

NEW METHOD FOR THE PREPARATION OF CESIUM.¹

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Received October 19, 1898.

WINKLER² tried to reduce cesium carbonate with metallic magnesium, in both glass and porcelain tubes in a current of hydrogen. He, however, obtained no cesium. Beketoff³ 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

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

² *Ber. d. chem. Ges.*, 23, 53.

³ *Bull. Acad. Petersburg*, 4, 247.