DIRECT TEST FOR CALCIUM IN THE PRESENCE OF BARIUM AND STRONTIUM.

By MALVERN W. LLES, Ph.B., School of Mines, Columbia College.

IN Douglas and Prescott's qualitative analysis, the following is given as a distinctive test for calcium in the presence of barium and strontium:

Ferrocyanide of potassium precipitates ferrocyanide of calcium and potassium, K_2CaC_4 , white or yellowish-white, soluble in 800 parts of cold or 145 parts boiling water, which slowly decomposes it, more soluble in dilute than concentrated hydrochloric acid. Barium and strontium are not precipitated by this reagent.

The reaction will be as follows:

On repeatedly trying the above, no such reaction was obtained, even in strong solutions of calcium chloride; which solutions were much more concentrated than the qualitative student will ever have in the regular course of analysis.

I began a series of experiments, in hopes of modifying this test for qualitative work; since the test, as now stated, I regard as utterly worthless and deceptive. The result of the investigation led to the following modification which is quite delicate.

To the filtrate from the ammonium sulphide group add ammonium chloride, ammonium hydrate, and ammonium carbonate, as usual, slightly wash the precipitate to free it from magnesium salts, which might be present, dissolve the precipitated carbonates upon the filter-paper with as small a quantity of dilute hydrochloric acid as possible. Next add to the hydrochloric acid solution potassium ferrocyanide, then ammonium hydrate, and heat to boiling; a slight precipitate of calcium, strontium, or barium carbonate may occur at this point from the carbonic acid contained in the ammonium hydrate; let the solution nearly cool and add acetic acid to strong acid reaction; if there is anything more than a trace of calcium present, a white coloration to a yellowish-white soon makes its appearance, generally at the top of the test-tube, soon spreading, however, throughout the entire liquid, and in a few minutes there will subside a white precipitate, rather granular in nature. If, however, only barium and strontium are present, the liquid will become clear, since the carbonates of these metals are soluble in acetic acid.

Owing to the strong affinity of ammonium hydrate for carbonic oxide, which it readily takes from the air, it may be generally assumed a precipitate will occur on the addition of ammonium hydrate to a solution containing either a barium, strontium, or calcium salt. Magnesium salts interfere with this test, hence it should be removed as above indicated. After the addition of acetic acid, care must be taken not to heat the solution, as I find the potassium ferrocyanide is decomposed by acetic acid, at a temperature between 130° and 140° F., and the result is a white coloration that might be easily mistaken for the calcium precipitate.

Frequently after the addition of potassium ferrocyanide and ammonium hydrate to a quite concentrated solution of either barium or strontium chloride, there settles a fine shiny crystalline salt, but which is entirely unlike the white cloud noticed when calcium is present.

Owing to the completeness and the degree of readiness with which calcium separates from a liquid when treated as above indicated, I am inclined to the opinion that the formula, $CaK_2FeC_4 + 3H_2O$, does not express the true composition of the precipitate in question. If by chemical analysis the salt is found not to be different from the above formula, then potassium calcium ferrocyanide is remarkably insoluble in ammonium acetate, which, it will be noticed, is formed in the mode of procedure given above.

PROPERTIES OF POTASSIUM CALCIUM FERROCYNIDE.

Storer states this salt is soluble in 795 parts water at 150° C., and 145 parts boiling water.

Since the solution in boiling water is a different color from that obtained in the cold, and since it yields no precipitate on cooling, decomposition has occurred. The salt is also decomposed by long washing with water. This salt is soluble in dilute hydrochloric acid, but concentrated hydrochloric acid precipitates it unchanged. It is soluble in nitric acid (sp. gr. 1.2, Mosander). Insoluble in ammonium chloride (H. Rose, Tr.).

RESUME OF TEST.

To a neutral or slightly acid solution that may contain barium, strontium, and calcium, add:

- 4 K₂Cy, Fe Cy₂ + NH₄HO—heat to boiling, and let nearly cool.
- Add H₂C₂H₃O₂ to strong acid reaction; a white precipitate indicates calcium.

CONCENTRATED SOLUTION OF SALICYLIC ACID.

By C. L. MITCHELL.

A STRONG solution of salicylic acid, for convenience in both dispensing and prescribing, has long been a desideratum, and until recently no practical way of overcoming the difficulty has been known.

Salicylic acid itself is very sparingly soluble in cold water, and though readily dissolving by the aid of heat, nearly all separates on cooling. Its alcoholic solution is not adaptable to the purpose—for when diluted with water, the acid immediately separates.

Various methods have been recommended for rendering the acid more soluble—namely: the use of various salts, such as sodium orthophosphate, calcium chloride, ammonium acetate, etc.; and also by dissolving it in glycerin. None of these modes of procedure give a solution which contains more than 1 per cent salicylic acid. The desideratum seems to be a concentrated solution which will bear dilution with water to any extent. Recently, a writer in the *Druggists' Circular* has recommended the use of sodium biphosphate and glycerin in the proportions of 1 part each of salicylic acid and the biphosphate to 16 parts glycerin. This gives a solution containing about 6 per cent salicylic acid, and is freely miscible with water in all proportions.

While recently experimenting with this formula, it occurred to the writer that probably a still stronger and more concentrated solution might be obtained by some slight modifications. After several experiments the following formula was adduced:

Acid, salicylic, pur..... 3 ij
Sodium biphosphate..... 3 j
Glycerine..... q. s.

Mix the acid and borax with f₃ iv glycerin, heat gently until dissolved, then add q. s. glycerin to make the measure f₃ i. This solution contains 25 per cent salicylic acid, and can be

diluted with either glycerin, alcohol or water to any degree desired.

The advantages of a concentrated solution of this description can scarcely be overestimated, as it affords a very convenient mode of both prescribing and dispensing salicylic acid.—*Am. Jour. of Pharmacy*.

SALICYLIC ACID.

By CHARLES BECKER.

THE addition of the phosphates of ammonium or sodium has been recommended to increase the solubility of salicylic acid in water, but these agents really amount to but very little, as a solvent of one part of the acid in three of either phosphate, and fifty parts (by weight) of water throws down a precipitate in less than twenty-four hours. An addition of two parts of sulphite of sodium to one of salicylic acid, in fifty parts of water, precipitates in a few hours. Borax, in the proportion of two parts to one of salicylic acid, and fifty of water, precipitates slightly after twenty-four hours; a solution of one part each of salicylic acid and borax, in five parts of glycerin and twenty-five of water, is permanent; while the same proportion of borax, acid and glycerin, in fifty parts of water, will precipitate after twenty-four hours. A solution of one part of acid to two of borax, in twelve parts of glycerin, made with heat, is permanent; but when one part of this solution is diluted with three parts of water, which makes it two parts of salicylic acid, four of borax, twenty-four of glycerin and ninety of water, a cloudiness appears in a few hours. One part of salicylic acid with one part of water of ammonia (20°) forms with ten parts of water a permanent solution; this has a light-brownish color, a very faint odor of ammonia, a very distinct, sweet taste of the acid, and a slight acid reaction on litmus paper.

Salicylic acid is soluble in ten times its weight of dilute alcohol, at a temperature of about 80° F., in one and a half times its weight of alcohol (0.835 sp. gr.), and in twice its weight of sulphuric ether. It is nearly insoluble in cold oil of turpentine, but hot turpentine dissolves about 5 per cent of its weight. Its alcoholic solution has a decided acid reaction on litmus paper. An addition of one fifth of one per cent of salicylic acid to aqueous infusions will preserve them for weeks; and the same proportion added to syrups made with fruit juices, while it will not arrest fermentation after such has set in, will prevent the same.

The acid used in the above experiments was of Schering's make, and perfectly white and inodorous.

When one part of salicylic acid and two parts of olive-oil are heated together they form a homogeneous mixture, admirably adapted for application to surfaces. The oil will separate to some extent on standing for a time, but agitation will easily combine it again.—*Am. Jour. of Pharmacy*.

NEW PROCESS FOR DETERMINING ASTRINGENTS.

By M. F. JEAN.

THE author has observed that astringents mixed with an alkaline carbonate absorb the solution of iodine with a readiness like that of the arsenite of soda. This absorption is directly proportional to the quantity of astringent matter present, 1 part of dry tannic acid taking up 4 parts of iodine. The solution of iodine required for the titration of tannin is obtained by dissolving 4 grms. of iodine in iodide of potassium, and making up the solution to 1000 c.c. with distilled water. To standardize this solution, place in a precipitating glass 10 c.c. of a solution of tannin containing 0.1 gm. per cent, add 2 c.c. of an alkaline solution containing 25 per cent of crystalline carbonate of soda, and then with a graduated burette drop the solution of iodine into this mixed liquid till a drop of the mixture, taken up with the stirring-rod, and placed upon a leaf of starch-paper, produces a very slight violet spot, which indicates the presence of free iodine and the end of the operation. The value thus obtained must be corrected—that is to say, from the number of c.c. of solution of iodine corresponding to 0.1 gm. of tannin must be deducted the volume of the solution required to produce the colored reaction upon starched paper. For this purpose 10 c.c. of distilled water are measured out, mixed with 2 c.c. of alkaline solution, and the solution of iodine is then added, drop by drop, till a spot is obtained upon the starched paper. With a solution containing 4 grms. iodine per litre the correction is generally 0.1 c.c. for a volume of 10 to 12 c.c., but the greater or less purity of the carbonate of soda may make a slight variation in this correction. To 0.01 gm. of tannin dissolved in 10 c.c. of water it is generally necessary to take 10.5 c.c. of a solution at 4 per 1000. The paper used is white filter-paper, covered by friction with a slight layer of powdered starch. For ordinary determinations tannic acid may be taken as the type of the active principle of astringent bodies. But if a high degree of accuracy is required, the solution should be standardized with a pure sample of the astringent body under examination, catechuic acid being used in case of catechu, morintannic acid for fustic, etc. Crystalline gallic acid decomposes the solution of iodine in the same proportion as tannic acid. If it is desired to determine these acids separately, we first find the joint amount of tannic and gallic acids, and then, operating on a fresh portion, remove the tannic acid by means of rasped hide or gelatin and alcohol, and determine afresh the gallic acid remaining. The tannic acid is then found by subtracting the second result from the first. The extractive matters found in astringents do not interfere.

RUSTING OF IRON.

By A. WAGNER.

DETAILS are given of experiments made upon strips of iron which were acted upon by water containing various salts, in presence of air free from carbon dioxide, and of air containing that gas at various temperatures, and also in sealed tubes, from which air was expelled.

The general results were that pure water in presence of air causes iron to rust; that if carbon dioxide is also present, the rusting is more rapid; that the production of rust is materially increased by the chlorides of magnesium, ammonium, sodium, potassium, barium and calcium, the first mentioned being most active in this respect; that iron immersed in evaporated river-water rusts more slowly than iron in distilled water; that the presence of oils or fats greatly diminishes the rapidity of rusting; that alkalies prevent the rusting entirely. Magnesium chloride solution, in the absence of air, attacked iron at a temperature of about 100°; chlorides of sodium, potassium, barium and calcium were without action under the same circumstances. The original paper must be consulted for details and measurements.—*Jour. Chem. Soc. [Lond.]*.

METALLIC CERIUM, LANTHANUM, AND DIDYMIUM.

Drs. HILLEBRAND and NORTON, in Bunsen's laboratory, have obtained, by the electrolysis of the cerium, lanthanum and didymium chlorides, the metals in quantities sufficient for careful investigation. As proof of the purity of the materials employed they refer to the methods of separation given by Bunsen (*Pogg. Ann.*, clv. 366).

CERIUM.

Metallic cerium has the color and lustre of iron; it slowly tarnishes in dry air, and in moist air soon changes color, as steel does when heated, to yellow, blue, and gray. After fusion it has the hardness of calcite, and is malleable and very ductile. The specific gravity of the electrolytic metal is 6.628, and after fusion under salt and potassium chloride it is 6.728. The low specific gravity found for cerium reduced by sodium 5.5 indicates that it contained sodium. The melting point of cerium is lower than that of silver, and considerably higher than that of antimony. Its kindling temperature in air and oxygen is much lower than that of magnesium. Pieces scratched off inflame, and the wire ignited in a flame burns more brilliantly than magnesium wire. It burns when heated in chlorine, less readily in bromine vapor, and without incandescence in iodine vapor. Water at common temperatures is slowly decomposed by it; cold concentrated sulphuric acid and cold red fuming nitric acid do not attack it, but these acids when dilute, and also hydrochloric acid, dissolve it.

LANTHANUM.

Metallic lanthanum is much like cerium in its general chemical deportment, but by concentrating nitric acid it is easily attacked. It is slightly harder and less ductile than cerium; it is less permanent in air, and even in dry air its color soon changes to a steel blue. The specific gravity of a piece deposited by electrolysis weighing 7.6 grammes was 6.163; after fusion it was less, 6.049. Its melting point appears to be near that of cerium, and its kindling temperature is higher. Small pieces from filing or striking on flint do not ignite spontaneously in the air, but burn brilliantly in the flame. Their analysis shows less than one per cent of impurity in the specimen.

DIDYMIUM.

Metallic didymium is more like lanthanum than cerium; it is not less lustrous, ductile or permanent in air than lanthanum, and has about the same hardness; its color is not as white, and moist air turns it yellow. Fine particles of the metal do not ignite spontaneously in the air, but burn when heated in a lamp flame. It is less fusible than either lanthanum or cerium, and the metal after fusion has a specific gravity of 6.544.—*Pogg. Ann.*

ANILINE GREEN IN TISSUES WITH COTTON WARP.

By preparing the tissues with sumach and salt of tin, they may be dyed in a solution of aniline green, but such dyeing in general wants body, and the tint is too bright for this kind of fabric. In practice these greens are generally obtained by first giving the cotton a tint of Prussian blue, and the wool one of indigo, and bringing them towards green by means of yellow wood or quercitron. The alkaline blues, called "Nicholson's blues," produce those tints more simply, for these blues take well on cotton; still, as the wool takes the color much more rapidly, it is well to mordant slightly with sumach or alum.

The following is the method recommended: For 10 kilogrammes of tissue, steep it for five or six hours in a decoction of 2 kilogrammes of sumach, then pass it cold through a solution of 1 kilogramme of alum. Then the dye vat being prepared with borax and Nicholson's blue, as for woollens, commence dyeing at tepid heat, and keep it 30 to 45 minutes with the temperature but slightly heated. During this time the cotton will take more than the wool. When the required tint is nearly obtained then the heat must be raised, in order that the color may be solid throughout.

In order to ascertain, if it be so, a small sample is steeped in very weak sulphuric acid, and the brightening of the blue furnishes the test.

After the fabrics are withdrawn from the blue dye they are well drained, and then steeped in a solution of 2 kilogrammes of alum, and 100 grammes of flavine. Dye tepid until the cotton seems sufficiently tinted, then raise the heat, and add cream of tartar 2 kilogrammes, and flavine 100 grammes. Immerse and boil till the tint required is obtained. The color, which before was dull and gray, is developed and rendered brilliant by this last operation. Finish by rinsing.—*Moniteur des Fil et Tissus*.

METALLIC GLOSS FOR DYED FABRICS.

WITH various varieties of goods and stuffs, it is often desired to give them a certain lustre or metallic gloss. A number of processes have already been introduced in the finishing treatment of such goods. The present receipt (recommended by the *Centralblatt für die Textil Industrie*) distinguishes itself by its adaptability to woollen and cotton fabrics, and by its ensuring better and handsomer results. Inasmuch as the glossing or lustring takes place with the dye manipulation, this process may likewise be said to be considerably cheaper than other processes. Supposing that the fabric to be treated is to receive a black or brown metal gloss, the treatment is as follows, after having damped the material with a weak solution of soda.

Two cloth pieces, black, 35 lbs.—Having dissolved 12 lbs. of green vitriol, 3 lbs. of blue vitriol, and 23 lbs. of pyrotartaric acid in a pan, the pieces are dipped in and allowed to boil well for one half hour. The cloth is next taken to the washing machine, or, better, to running water, and then dyed in the usual way in logwood, etc. After rinsing, the cloth is next dipped into a warm bath (65 deg., 88 deg. C.), composed of 5 lbs. blue vitriol, dissolved in 12 lbs. of ammonia, with the necessary quantity of water. After rinsing once more, the cloth is changed to a hyposulphite of soda solution (10 lbs. of hyposulphite of 1200 specific gravity, with the addition of water), after which it is taken out, washed, and finished in the usual manner. The cloth may be allowed to remain one quarter of an hour in each of the two last-mentioned baths.

If a brown metallic gloss be desired, the cloth is dyed to pattern, washed and passed through two baths of blue vitriol, dissolved in ammonia, and removed to the hyposulphuric soda solution. In cases where the metallic gloss is to be gray, lavender blue, or of other similar colors, in place of the copper salt, substitute a lead, zinc, or silver salt, allowing the fabric to be likewise latterly subjected to the hyposulphuric soda solution.