

price includes basket, ropes, sandbags, drag, and other accessories of military balloons.

A detachment of Signal Corps Sergeants will be sent to the Exposition grounds to join the force already there, that practical illustration may be given of the methods of signaling in the army, including the operation of this military balloon. It is said that this will be a "regulation, globular, captive balloon," attached to the basket of which is a light wire, extending to a huge reel, which allows the wire to unwind as the balloon ascends, and serves to pull the balloon back to camp. The wire has a double use, in holding the balloon and furnishing the occupants of the basket a means of communicating, as by telephone, with the officers at the reel.

**Indiana's Coal Exhibit.**—The Indiana coal operators have arranged to make an elaborate exhibit, the block coal interests to be represented by the Brazil Block Coal Company, and the bituminous mines by the Foley Mine. The latter was agreed upon for the reason that it can furnish a larger block of coal than any of the other bituminous mines, owing to the mine's lesser depth. The block of coal from the Foley Mine will be over 7 ft. in height. The other mines in this vicinity will also make exhibits. The Hocking Valley will have on exhibit a block of coal showing a vein 16 ft. 3 in. in height, and New South Wales will have coal from 10-ft. veins, but the latter, owing to the presence of sulphur, is not so good as either the Hocking Valley or the coal of this district. Governor McKinley has placed Ohio's coal exhibit in charge of the State Mine Inspector, and the operators of this State will urge Governor Matthews to put Mine Inspector McQuade in charge of Indiana's exhibit. It is believed that such a plan would largely enhance the merits of an industry that is second to none in the State's wealth.

## CONTRIBUTIONS TO PRACTICAL RAILROAD INFORMATION.

### Chemistry Applied to Railroads.

#### SECOND SERIES.—CHEMICAL METHODS.

#### II.—METHOD OF DETERMINING FREE CAUSTIC AND CARBONATED ALKALI IN SOAPS.—*Continued.*

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(Continued from page 200, Volume LXVII.)

#### NOTES AND PRECAUTIONS.

It will be observed that the method above given for determining carbonate of soda in soaps is based on the insolubility of this salt in a solution of soap in absolute alcohol, and that the method for getting the free caustic alkali dissolves the soap in presence of an acid which cannot decompose it, which has but slight action on the carbonate present, and which combines with the free caustic alkali as fast as solution takes place, and enables this constituent and the small amount of carbonate dissolved to be measured.

Positive experiments show that with good absolute alcohol, and with soap which has been freed from water, the carbonate determination is very sharp, the salt being almost absolutely insoluble. Many soaps in the market, however, contain from 5.00 per cent. to 35.00 per cent. of water, and if in addition to this water in the sample 95.00 per cent. alcohol only is used, the solubility of the carbonate of soda becomes quite perceptible. The error in these cases may amount to from 0.10 per cent. to 0.30 per cent. Many of the common soaps contain as high as from 5.00 per cent. to 7.00 per cent. of carbonate of soda, and in such samples this error may perhaps fairly be ignored. Whether absolute alcohol or 95.00 per cent. alcohol is used, it is always desirable to dry the soap, and if this is done, the error, even when 95.00 per cent. alcohol is used, is not much over 0.10 per cent. It is believed that if the directions are closely followed in every respect, the error can always safely be ignored.

The solubility of soap in absolute alcohol is apparently not quite as great as in 95.00 per cent. alcohol, and therefore after solution is complete, filtration must proceed with moderate rapidity, or the solution may gelatinize and clog the filter. There is less danger of this the hotter the solution is kept.

If the soap under examination contains uncombined fat acid along with carbonate of soda, as is frequently the case in olein soaps, combination may take place between these constituents in the boiling absolute alcohol solution, and consequently the analysis may be in error to this extent. We do not know of any method of overcoming this difficulty.

The drying of soap is a slow operation at best. It is facilitated by having the shavings very thin, and by having the temperature of the air surrounding the soap at first not hotter than 120° Fahrenheit, and gradually, as the drying proceeds, raising the temperature to not above 200° Fahrenheit. Of course the soap must not be melted, as this would endanger the combination of some of the free or carbonated alkali with free fat, if any were present. Experiments indicate that if the amount of water in the dried soap does not exceed 5.00 or 8.00 per cent., the resulting error can be ignored.

The stearic acid solution, as made from commercial materials, is sensitive to changes of temperature. It is, therefore, essential to prevent it from becoming too cold, or its strength will be diminished by something crystallizing out.

Most of the commercial 95-per cent. alcohol does contain, and the absolute alcohol may contain small amounts of free acid of some kind—probably acetic. The amount of this can readily be determined by the use of standard alkali, and in the carbonate determination this acid must of course be allowed for.

Much of the phenolphthalin of the market apparently contains something which combines with alkali without showing change of color. If this is not satisfied with alkali as directed, the reaction will not be quite so delicate.

We make standard sulphuric acid solution by adding to a clean, clear glass 5-gallon bottle, 15 liters of distilled water, and then weigh out and add to it 397.5 grams of concentrated C. P. sulphuric acid. It is better to set the water in the bottle in motion by stirring with a clean glass rod before adding the sulphuric acid. After the acid is in, it is essential to agitate thoroughly by stirring and shaking, but not advisable to draw air through for this purpose, as this causes the liquid to take up carbon dioxide, which interferes with its subsequent usefulness with phenolphthalin. It is not desirable to standardize on the same day, both on account of temperature and also because, if we may trust our experience, it is very difficult by any practicable method of agitation to get so large a bulk of liquid entirely homogeneous without standing. If the first standardizing shows that it is essential to add say 750 c.c. of water, we usually add only 700, since we expect to standardize once more any way, and too much water must of course be avoided. The second addition of water is usually less than 100 c.c. We regard both agitation and standing over night essential after each addition of water.

We make caustic potash solution in the same kind of bottle and in the same amount as the acid solution. The same precautions should be taken in regard to stirring, and allowing to stand over night, as in the case of the acid. It is well known that caustic potash solution, if properly made as above described, contains a small amount of caustic lime in solution. Of course this lime will appear in the comparison with the standard acid. If now the water used in the first addition contains a little carbon dioxide, a little of the lime will be precipitated on standing over night, and weaken the solution a little. It is therefore not advisable to add quite as much of the water shown by calculation the first time, as in case of the acid.

We make the two solutions, as will be observed, in quite large amounts, and take considerable pains to have them right, since other work depends upon them. The bulk above described lasts us four or five months. Both of the solutions are kept on a shelf somewhat higher than the burettes, and both are drawn into the burettes by means of glass tube siphons with glass cocks at the lower ends. In accurate work it is of course essential to draw out and throw away the liquid which has been standing exposed between the cock and lower end of the siphon tube before filling the burette. The air which goes in to replace the liquid in the large glass bottles should bubble through caustic potash solution in order to keep out carbon dioxide. We use potash bulbs for this purpose.

The fact that phenolphthalin is sensitive to carbon dioxide in water solution, and to carbonates and bicarbonates, may lead to serious error unless sufficient care is taken to add enough acid to decompose all carbonates and bicarbonates and then expel the gas by boiling before subsequent titration with caustic potash. An illustration will make the matter clear. Let

us suppose that in obtaining the relation between carbonate of soda and sulphuric acid in standardizing the acid, the carbon dioxide is not quite all removed by boiling, when we attempt to measure the excess of the acid by means of the caustic potash solution. We add this solution drop by drop, and ultimately reach a point when all the free sulphuric acid is satisfied with the caustic potash; but since phenolphthalein in presence of carbonic acid or carbon dioxide in water solution does not change color until part, at least, of this carbonic acid is also satisfied with caustic potash, we do not get our end reaction when the sulphuric acid is all satisfied, as should be the case, but rather after some further addition of caustic potash. The error is obvious; and if we may trust our experience, there is always uncertainty if carbon dioxide or carbonates are present when using phenolphthalein as indicator. Even carbon dioxide in the standard sulphuric acid solution or carbonates in the caustic potash solution will cause difficulty. Methyl orange, and possibly other indicators, do not give so much trouble from this cause; but all that we have ever tried are so much less sensitive and sharp at the end reaction than phenolphthalein, provided the conditions are right, that we prefer to take the extra trouble. Furthermore, positive experiments show that if the solution is rendered clearly acid with standard acid and boiled for 10 minutes or even less, the carbonic dioxide will all be expelled; so that we think if the directions are closely followed the results will be fairly accurate. It is obvious that if the distilled water used in making the standard acid contains carbon dioxide, there will always be some present, with a consequent liability to uncertainty in the final results. Presence or absence of carbon dioxide in the standard acid can be proved by titrating some of the acid cold with standard caustic potash, using phenolphthalein for indicator, and then titrating another similar portion after it has been boiled. If carbon dioxide is absent, the two tests should show the same figure. If it is present in injurious amount it will be essential to always boil to expel carbon dioxide in all tests where this acid is used before attempting to titrate in presence of phenolphthalein.

It is obvious if a soap contains more free alkali than is sufficient to combine with all the stearic acid in 100 c.c. of the stearic acid solution taken, it will be necessary to either use more of the stearic acid solution or diminish the amount of soap to start with.

If a soap has silicate of soda in it, this apparently breaks up in the stearic acid solution, part of it counting as caustic soda and part of it remaining behind on the filter, possibly as insoluble acid silicate of soda. Borate of soda also breaks up in the stearic acid solution, and part, at least, of the base counts as free caustic alkali. We have never carefully investigated the behavior of these substances in the absolute alcohol solution, as, if either of them are present in any perceptible amount, the soaps would not fill our specifications.

It will be observed that in the calculations the results are reported in terms of soda salts. This is because our specifications for soap are so drawn. Of course the results could be reported in potash salts equally well.

We usually calibrate burettes by filling them with distilled water at about 70° Fahrenheit, and then draw out into a flask, and weigh each 5 c.c. to the bottom, and then fill again and start 1 c.c. lower down, and proceed as before. Two or three times through in this way will check any discrepancies that will seriously affect the result. Of course each 5 c.c. should increase the weight 5 grams, and if the burettes are fairly well graduated the differences should not be over the weight of one drop, approximately 50 milligrams. Obviously by using a good balance and going through the burette times enough, the calibration can be made as fine as the graduation. We do not, however, regard this as necessary. It is hardly necessary to add that the burettes to be used with the standard acid and alkali must be alike, or, indeed, interchangeable.

It is well known that change of temperature affects all volumetric work, and it is equally well known that there is no error from this cause if the solutions are used at the same temperature at which they are standardized. We usually keep our standard solutions on a shelf near the ceiling of the room, where the temperature is about 80° Fahrenheit, and standardize them finally after they have been at this temperature over night. With most of the determinations for which we use these solutions, a change of temperature of 10° Fahrenheit does not introduce a greater error than would be produced by one drop of the solution in excess. As we cannot work closer than one drop, except by using weaker solutions, the error of temperature is usually ignored. Of course in very fine work care should be taken to use the solutions at the temperature at which they are accurate.

It is of course well known that other materials than carbonate of soda have been recommended as the starting-point in

making acid standard. It is entirely possible that some of these are better than carbonate of soda, but it is believed that if the directions are closely followed, the results will be fairly accurate.

The use of stearic acid to combine with and measure the free caustic alkali in soaps is believed to possess advantages which do not inhere in other acids. First, the solution keeps unchanged almost indefinitely, which is not the case apparently with oleic, and possibly not with palmitic, both of which, as well as stearic, may be constituents of soap, and both of which might possibly be used in place of stearic. Second, the soap apparently not being decomposed, no question can arise as to whether recombination takes place in the same way during the subsequent titration. Third, stearic acid is so weak that its action on carbonate of soda, even in boiling alcoholic solution, is slow and if the soap is cut in quite thin layers, and titration takes place as soon as solution is complete, the carbonate dissolved does not amount to more than 0.25 per cent. Fourth, many of the strong mineral acids act on the organic constituents of the soap, and hence their use is inadmissible. Also all the stronger acids, even organic ones, dissolve carbonate of soda quite readily, as well as decompose the soap.

It is obvious that there may be a number of conditions in soaps obtained in the market. First, there may be an excess of unsaponified fat, arising from failure of the soap-maker to use enough caustic alkali. In this case, if there is also no carbonate present, the method as described above shows nothing; that is, the titration of the stearic acid at the end of the operation gives the same figure as the titration of the stearic acid alone. We have had cases of this kind happen in our experience. It is obvious that the addition of a known amount of alkali in alcohol to a case like the above, with subsequent boiling and determination of the excess of alkali, would give the amount of unsaponified fat present. We have not experimented with this, however. If carbonates are present, some of the stearic acid would be used up, since this acid in boiling alcoholic solution acts slowly on carbonates, and it would require a carbonate determination as described before it could be stated that the soap is free from caustic. This statement of course involves the idea that unsaponified fat in a soap is not decomposed by carbonate of soda in boiling absolute alcohol solution, as described in the carbonate determination. We have not proven this, however, our experiments only showing that carbonate of soda is insoluble in a boiling solution of soap in absolute alcohol. It would almost seem safe to conclude from this, however, that since carbonate of soda is insoluble, it could not act on free fat. Second, there may be an excess of free fat acid in the soap, owing to the same reason as before—viz., failure to add enough alkali. This is liable to be the case with soaps made from rosin, and in the so-called olein soaps. In this case the method as described, if no carbonates are present, enables the amount of this free fat acid to be determined. The titration of the solution actually gives a higher figure than the stearic acid alone, the excess of course being due to the free fat acid in the soap. We have had many cases of this kind. If carbonates are present in amount just sufficient to satisfy the free fat acid in the soap, and if the boiling is continued long enough so that these carbonates are just decomposed, neither the method for determining carbonate nor that for determining caustic will reveal this fact. For all other proportions of carbonates along with free fat acid in a soap, the methods given enable close approximations to the facts to be obtained. Third, there may be free caustic alkali along with free unsaponified fat. In this case, whether carbonates are present or not, the methods as given are applicable, and give the actual state of affairs in the soap. Fourth, there may be free caustic alkali along with free fat acid. In this case, if carbonates are not present, and if the amount of caustic is just sufficient to satisfy the free fat acid, neither of the methods reveal the facts, since the free fat acid and free alkali would combine on solution of the soap. For all other proportions of free caustic alkali an approximation to the state of affairs may be obtained by the methods as given. If carbonates are present along with free fat acid and free caustic alkali, and if the amount of both of these is just sufficient to satisfy the free fat acid, neither of the methods reveal the facts. For all other proportions the same remarks apply as above. Fifth, there may be free caustic alkali along with normal soap. In this case, whether carbonates are present or not, the methods are applicable, and reveal the state of affairs. It is obvious from the above discussion that soaps containing free fat acid along with just enough caustic and carbonated alkali to combine with the free fat acid cannot be successfully examined by the methods given. It is believed that in all other cases the methods given enable a satisfactory opinion to be expressed in regard to the soap.

(TO BE CONTINUED.)