

THE SECRETS OF NATURAL AND ARTIFICIAL CHEMISTRY



Benzoic acid, as it exists in the resin, is the natural production of the plant from which the resin is derived. It may also be produced artificially. Abel found that when cumole was treated with nitric acid, so dilute that no red vapors were evolved for several days, this hydro-carbon was converted into benzoic acid. Guckelberger has, by the oxidation of casein with peroxide of manganese and sulphuric acid, obtained as one of the products benzoic acid. Albumen, fibrin, and gelatin yielded similar results when treated as above. Wöhler has detected benzoic acid in Canadian castor, along with salicin. It is also formed by the oxidation of the volatile oil of bitter almonds. Benzoate of potash results when chloride of benzoyle is treated with caustic potash.

Benzoic acid in the animal economy is converted into hippuric acid, which may by the action of acids, be reconverted into benzoic acid. Benzoic acid should be completely volatile, without leaving any ash or being carbonized when heated. When dissolved in warm water, to which a little nitric acid has been added, nitrate of silver and chloride of barium should produce no precipitates. Oxalate of potash should give no turbidity to an ammoniacal solution of this acid. When heated with an excess of caustic potash it should evolve no smell of ammonia, otherwise, it has been adulterated with sal ammoniac. In spirit, benzoic acid is easily soluble, and requires parts of cold and 20 parts of boiling water to dissolve one part of it.

Chemists possess only a very incomplete knowledge of the coloring matters of flowers. Their investigation involves difficulties which cannot be mistaken. The matters which color flowers are uncrystallized; they frequently change by the action of the reagents employed for their preparation; and, also, very brilliantly colored flowers owe their color to very small quantities of coloring matter. On the nature of the coloring matters of flowers several opinions have been expressed.

Some observers have assumed that flowers owe their color to only two coloring matters, one of which is termed anthocyan, and the other anthoxanthine. Others will find a relation between the green coloring of leaves, the chlorophylle, and the coloring matters of flowers. They support their opinion generally on the results of the elementary analysis of those different bodies; but all chemists know that chlorophylle has not yet been prepared in a pure condition. Probably, it retains various quantities of fatty and albuminous bodies.

Further, the coloring matters of flowers are scarcely known, so that it is impossible to establish relations supported by the necessarily uncertain composition of impure bodies. Some time since the blue color of flowers was ascribed to the presence of indigo; but Chevreul has shown, in a certain way, that the blue substance of flowers is always reddened by acids; and that with indigo it is quite different, which, as is known, retains its blue color even when the strongest acids are allowed to act on it. It is thus seen that the coloring matters of flowers have heretofore only in a superficial manner been examined, and that it is important to again undertake their complete examination, as these bodies are interesting to the chemist, because they are employed as reagents in the laboratory for the recognition of alkalies; and by an improved knowledge of them the florist might find the way by which he could give to cultivated flowers various colors.

We have believed that before undertaking their elementary analysis, methods must be carefully sought for which can be followed for the obtainment of the coloring matters of flowers, and that it should be proved whether these substances are to be considered as independent bodies, or whether they proceed from one and the same matter, which is changed in various ways by the juices of the plant. We now publish the results of our first investigations. Blue Coloring Matter of Flowers (Cyanine).—The blue coloring matter of flowers we propose to call cyanine. To obtain this substance we treat the petals of *Centauria cyanus*, *Viola odorata*, or *Iris pseudacorus*, with boiling alcohol, by which the flowers are decolorized; and the liquid acquires immediately a fine blue color.

If the coloring matter is allowed to remain some time in contact with alcohol, it is perceived that the blue of the liquid gradually disappears, and soon a yellow brown coloration takes its place. The coloring matter has in this case suffered an actual reduction by the prolonged action of the alcohol, but it will again assume its original color when the alcohol is allowed to evaporate in the air. Nevertheless, the alcohol must not be allowed to remain in contact too long with the coloring matter, because the alcoholic extract will not then again assume its blue coloration by the action of oxygen. The residue remaining from the evaporation of the alcohol is treated with water, which separates a fatty and resinous substance.

The watery solution which contains the coloring matter is then precipitated by neutral acetate of lead. The precipitate, which possesses a beautiful green color, can be washed with plenty of water, and then decomposed with sulphuretted hydrogen; the coloring matter passes into the watery solution, which is carefully evaporated in a water-bath; the residue is again dissolved in absolute alcohol; and lastly, the alcoholic solution is mixed with ether, which precipitates the cyanine in the form of blue flocks. Cyanine is uncrystallizable, soluble in water and alcohol, insoluble in ether; acids, and acid salts color it immediately red; by alkalies it is, as known, colored green. Cyanine appears to behave as an acid, at least it forms with lime, baryta, strontia, oxide of lead, green compounds insoluble in water.

Bodies absorbing oxygen, as sulphurous acid, phosphorous acid, and alcohols, decolorize it; under the influence of oxygen its color is restored. We must here mention that Moroz has prepared a beautiful blue substance from *Centaurea cyanus* by treatment with absolute alcohol. Rose-red Coloring Matter.— We have employed alcohol to extract the substance which colors rose-red certain dahlias, roses, pœonias, For the procuration of this coloring matter the method pursued is exactly as that for the preparation of cyanine. By an attentive comparison of the properties of this coloring matter with those of cyanine, we have found that the rose-red coloring matter is the same as the blue, or at least results from a modification of the same independent principle.

It appears in the rose-red modification, when the juice of the plant, with which it exists in contact, possesses an acid reaction. We have always observed this acid reaction in the juices of plants with red or rose-red coloration, while the blue juices of plants have always exhibited an alkaline reaction. We have exposed most of the rose-red or red-colored flowers which are cultivated in the Paris Museum to the influence of alkalies, and have seen that they first become blue and then green by their action.

It is often perceived that certain rose-red flowers, as those of the Mallow, and in particular those of the *Hibiscus Syriacus*, acquire by fading a blue and then a green coloration, which change, as we have found, depends on the decomposition of an organic nitrogenous substance, which is found very frequently in the petals. This body generates as it decomposes ammonia, which communicates to the flowers the blue or green color.

By action of weak acids, the petals can be restored to their rose-red color. The alteration of color of certain rose-red flowers can also be observed when the petals are very rapidly dried, for example, in vacuo, by which it cannot be easily assumed that a nitrogenous body has undergone decomposition to the evolution of ammonia. But, before all things, it must be mentioned that in this case the modification of color passes into violet, and never arrives at green; and, further, that it is always accompanied with the evolution of carbonic acid, which we have detected by a direct experiment.

Petals which were before rose-red, and have become violet by slight drying, evolve carbonic acid, and on that account it may be assumed that the rose-red color is produced in the petals by this carbonic acid, and that by its expulsion the petals assume the blue color, by which the flowers with neutral juices are characterized. We believe that we are able to speak with certainty that flowers with a rose-red, violet, or blue color, owe their coloration to one and the same substance, but which is modified in various ways by the influence of the juices of plants. Scarlet-red flowers also contain cyanine reddened by an acid, but in such cases this substance is mixed with a yellow coloring matter which we will now describe. Yellow Coloring Matter.—The simplest experiments show that no analogy exists between the substance which colors flowers yellow and that of which we have already spoken.

The agents which generate so easily with cyanine, the rose-red, violet, or green coloration, cannot in any case impart these colors to the yellow substance obtained from flowers. By the examination of the various yellow-colored flowers, we have ascertained that they owe their coloration to two substances, which differ from one another in their properties, and appear not to be derived from the same independent principle. One is completely insoluble in water, which we have termed xanthine, a name which Runge has given to a yellow matter from madder. As this name has not been accepted in science, we have employed it to denote one of the coloring matters of yellow flowers. The other substance is very soluble in water, and is by us termed xantheine. Xanthine, or the Yellow Coloring Matter insoluble in water.—We have prepared this coloring matter from many yellow flowers, but chiefly from *Helianthus annuus*.

To obtain it we treat the flowers with boiling absolute alcohol, which dissolves the coloring matter in the heat, and by cooling almost completely allows it again to precipitate. The yellow deposit which is obtained in this way, is not pure xanthine, as it contains a rather considerable quantity of oil. To separate this oil we have recourse to a moderate saponification; thus, we heat the yellow precipitate with a small quantity of alkali to saponify the fatty body mixed with the xanthine, which even contains the xanthine dissolved. As the coloring matter is soluble in the soap solution, we do not treat the mass with water, but decompose it with an acid which isolates the xanthine and the fatty acids resulting from the saponification. This precipitate we treat with cold alcohol, which leaves behind the fatty acids, and dissolves the xanthine.

This substance is a fine yellow color, insoluble in water, but soluble in alcohol and ether, which are thereby colored golden yellow. It appears to be uncrystallizable, and possesses the general properties of resins. Xanthine, in combination with cyanine, modified by the various juices of plants, communicates in variable proportions orange-yellow, scarlet-red, and red colors to flowers. Xantheine, or the Coloring Matter soluble in water.—By the preparation of the substance which colors yellow certain dahlias, it is at once perceived that it has no analogy to xanthine. The latter is as known insoluble in water, while the coloring matter under consideration is readily soluble in water.

To obtain the xanthine we treat the petals of yellow flowering dahlias with alcohol, which quickly dissolves the yellow coloring matter, besides the fat and resin. The solution is evaporated to dryness, and the residue treated with water, whereby the fat and resin are separated. The water is again evaporated to dryness, and the residue treated with absolute alcohol. The resulting solution diluted with water is mixed with neutral acetate of lead, which precipitates the coloring matters.

The lead precipitate is then decomposed with sulphuric acid, upon which the xantheine which remains dissolved in the water is purified by alcohol. Xantheine is soluble in water, alcohol, and ether, but crystallizes from none of these solutions. Alkalies color it intensely brown. Its power of coloration is considerable. It dyes various fabrics of a yellow tone, which is without brilliancy. Acids again destroy the brown coloration produced by alkalies. Xantheine combines with most metallic bases, and forms therewith yellow or brown insoluble lakes.

The facts here related agree with all which has been previously observed regarding the coloring matters of flowers. It is known that blue flowers can become red, and even white, where their coloring matter is destroyed, but never yellow—and vice versâ. These three coloring matters can generate the colors either alone or by admixture, which are seen in flowers; but whether they are the only matters which color flowers, we are at present unable to determine. —Journal de Pharmacie.

This improved process consists of two parts:— the application of highlyheated steam to heat the fatty matters under treatment, by which means the requisite heat for melting these substances is obtained, and at the same time the atmosphere is thereby excluded; the heated steam so applied in its passage off, carries with it the offensive smells given off by the fatty matters, and being made to traverse a pipe or passage up or along which gaseous chlorine is allowed to flow, a complete disinfection of the offensive products is thereby effected. the treating of bees'-wax in a mixture of hard acid fat and bees'-wax, with compounds of chlorine and oxygen, preferring to employ that disengaged from chlorate of potash by treating it with sulphuric acid. For this purpose, takes at the rate, say, of a ton of yellow bees'-wax, and melts and boils it up with free steam for about half an hour.

It is then allowed to stand a short time, and is then decanted into another vessel provided with a steam-pipe to emit free steam; about. of chlorate of potash is added, and the steam turned on; of sulphuric acid, diluted with a like weight of water, is then gradually added. The matters are allowed to stand for a short time, and are then decanted into another vessel, and again boiled up with free steam, and treated with a like quantity of diluted sulphuric acid.

The bees'-wax is then decanted into a receiver, and is ready for use. The bees'-wax may, before undergoing these processes, be combined and boiled up with a hard fatty acid, and then treated as above described. Faiszt has submitted this celebrated shaving soap to analysis. He states that it is made by saponifying mutton fat with lime, and then separating the fatty acids from the soap thus formed, by means of a mineral acid. These fatty acids are afterwards combined with ordinary caustic potash to produce the Naples soap.

The removal of the duty from soap, and the consequent emancipation of this branch of industry from the tender mercies of the Excise, has given a fresh impetus to the manufacture of this important article of daily use, and enabled some processes to be practically carried out in England, which, previous to the removal of the duty, could not be adopted in this part of her Majesty's dominions. It will doubtless appear strange to those unacquainted with the circumstances, that owing to the mode of levying the duty by admeasurement, and not by actual weight, the maker of a particular kind of soap was debarred the privilege of manufacturing in this country.

Fortunately for him, the manufacture of soap being free from all Excise restrictions in Ireland, he was enabled to carry out his process in the sister kingdom, whence it was exported to England, and admitted here on payment of the Customs' duty, which was the same as the Excise duty on its manufacture here. All this roundabout method of doing business is now done away with, and no restriction now exists to mar the peace of the soap manufacturer. Amongst various new processes lately introduced is that of, which is practically carried out in the following manner:— Combine. of stearic or margaric acid, as free from elaine or oleine as possible, or palmatine, or any vegetable or animal stearine or margarine, at the temperature of ,with a solution of bicarbonate of potash or soda, specific gravity. Constantly stir or mix until an intimate combination is obtained, and that the elements will not part when tried upon glass or any other similar substance.

When the mass is cooled down to about. add one pound per cent. of liquor ammoniæ, specific gravity, and one pound per cent. of strongest solution of caustic potash; these are to be added gradually, and fully mixed or stirred until perfectly combined. Dissolve of common resin of commerce, by boiling it with a solution of subcarbonate of potash and common soda of commerce, in equal parts, as much as will give the solution a specific gravity of about, when boiling hot. Mix these perfectly with the above-mentioned stearic or margaric acids, and carbonated alkali; then add a strong solution of caustic potash or soda, until a perfect saponification is produced. The dose of caustic alkali will much depend upon the purity of the stearine or margarine employed.

The separation is now effected by using common salt, or sulphate of soda, as is known and practised by soap manufacturers. If the soap intended to be produced is to be colorless, no resin must be employed, and a larger dose of liquor ammoniæ and caustic alkali must be used, according to the dryness of the stearine matters to be operated upon.

In consequence of the ceremonious process by which the fatty acids are determined in one portion of the soap, and the alkali by the incineration of another, I consider the following method is not unworthy of publication, because it appears to afford quicker and more correct results by reason of the greater simplicity of the manipulation. It is available principally for soda soaps, which are the most common; but it may be also employed with corresponding alterations for soaps which have other bases. A piece of soap weighing two or three grammes is dissolved in a tared beaker glass of about cubic centimetres capacity with cubic centimetres of water, by heat, in a water-bath, and then three or four times the quantity of diluted sulphuric acid or as much as is necessary to decompose the soap, added from a burette.

When, after repeated agitation, the fatty acids have separated in a transparent clear stratum from the aqueous solution, it is allowed to cool, and then the contents of the beaker glass are placed in a moistened filter, which has been previously dried at. and weighed. The contents of the filter are washed until their acid reaction disappears. In the meanwhile the beaker glass is placed in a steam-bath, so that, it being already dry, may support the washed and partly dry filter, which is laid on the mouth of the glass as if it were in the funnel.

The fatty acids soon pass through the paper, and for the most part flow ultimately to the bottom of the beaker glass; the increase of weight of which, after cooling, and the subtraction of the weight of the filter, gives the quantity of fatty acids present in the soap. A second drying and weighing is not necessary, if on the cold sides of the interior of the glass no damp is to be observed, which is occasioned by a trace of water still present. If the quantity of oxide of iron added to marble the soap is considerable, it may be easily found by incinerating the filter and determining the weight of the residue.

The fluid runs from the fatty acids on the filter, which, with the washings, has been preserved in a sufficiently large beaker glass, is colored with tincture of litmus, and decomposed with a test alkaline solution until the blue color appears. The difference of the quantity of alkali required to neutralize the sulphuric acid, and the quantity of sulphuric acid used in the first instance, allows a calculation to be made as to the quantity of effective alkali in the soap, for example:— A determination of the alkali as a sulphate afforded in another portion of soap . of soda, because the sulphate of soda and chloride of sodium present in the soap gave up their alkali.

The alkaline fluid applied by me was a saccharine solution of lime, which can be naturally replaced by a solution of soda, and must be if the chloride of sodium and sulphate of soda mixed with the soap shall be determined in the following way:— The fluid again exactly neutralized with alkali is evaporated to dryness, and the residue gently heated to redness. As in the above manipulation, the fluid was not heated to the boiling point, the original chloride of sodium and sulphate of soda are contained in the weighed residue, besides the soda of the soap and that which has been added with the sulphuric acid, forming sulphate of soda.

A second exposure to a red heat with sulphuric acid converts the whole residue into sulphate of soda, and from the increase of weight, by a comparison of the equivalents of the quantity of the former may be decided. According to the equivalents which Kopp furnished in , the increase of weight to the chloride of sodium is as. The original sulphate of soda must be, lastly, found by the subtraction of the same salt formed plus the calculated chloride of sodium from the first heated residue.

In practice, it is seldom necessary to proceed with the determination of the chloride of sodium and sulphate of soda, except with stirred and cocoa-nut oil soaps; certainly less of the truth is seen if, after the above determination of the fatty acids and the effective alkali, the absent per centage of water is introduced in the calculation, than if the water is reckoned, which is never completely evolved from soap, even technically prepared at. And another determination made of the fatty acids or alkali en bloc the fatty acids, or even the alkaline contents.

The method here given partakes of the usual imperfections, that the fatty acids as well as the unsaponified soap are equally estimated, and the mixed hydrate or carbonate of the alkali as well as the combined alkali. The presence of the carbonate can be easily recognized by the foaming of the soap solution, upon the addition of the sulphuric acid. These imperfections, however, are of little importance. It must be granted that the minutely correct determination of the constitution of soap must be always yielded up to those who are technically conversant with this department of chemistry, the estimation of free alkali and unchanged fat excluded in, at least, by certain ages of the soap.

Further, a considerable excess of one or another ingredient soon betrays itself by a corresponding departure in the soap of the characteristic properties of a good product, and a small excess can be judged sufficiently exact from the proportion of the alkali, which, supposing soda present, should not amount to more than. with a pure cocoa-nut oil soap, not less than. with a tallow soap; but with palm oil and mixed soaps the one or the other limit approximates.—Journal für Praktische Chemie.

The fats which exist in nature can be divided into the general and the special; the former exist in almost all plants and parts of plants; the latter includes only some vegetable substances, as laurostearine, myristicine, and palmatine. The consistence of fats of the general kind depend upon the proportions of margarine, stearine, and oleine contained in them. The former preponderate in the solid fats (butter, lard, and tallow); and the latter in the fluid ones or oils. According as an oil contains oleic acid or olinic acid, it is termed a fatty or drying oil. To the class of fatty oils belong olive, almond, hazel-nut, beech, rape oils, to that of drying oils, linseed, nut, hemp, poppy, grape-seed, oils, which are used for varnishes.

In the vegetable kingdom the fats are chiefly in the seeds and in their coverings, seldom in the perispermium (poppy), and in the fleshy substance surrounding the seed (olive). The fat in the seed is mostly enclosed in cells with a proteine compound. In the animal kingdom certain parts of the body are quite filled with fat-cells, particularly under the skin (Paniculus adiposus), in the cavities of the abdomen, in the so-called omentum, in the kidneys and the tubulated canals of the bones. Fat is also enclosed in cells (fatty globules) in milk.