Mechanics, Physics, and Chemistry.

In the "Journal für Praktische Chemie," for May, 1843, an essay appeared by Carl Hochstetter, embracing a series of experiments on Sugar, subjected to various actions, and chiefly designed to develop the action of the substances contained in the juice of the Sugar-beet, as well as those with which the Sugar is brought in contact in the course of manufacture. The first part of the essay referring only to the Sugar-beet, we shall confine ourselves to the subsequent portion, which will apply to the manufacture of Sugar generally. J. C. B.

Behavior of pure solutions of Sugar under different actions and circumstances; by CARL HOCHSTETTER. Translated by OEHL-SCHLAGER, and communicated to the Journal of the Franklin Institute by Wm. M. Davis.

Both in the tropical and home manufacture of sugar, the sugar obtained by expression, or maceration, is only partially preserved in its original state, that is, as cane-sugar. Even before it had been proved to a certainty, that the sugar-cane, and the beet, contained only cane sugar, it was admitted that a large portion of the molasses of the sugar refiner, is to be attributed to a change of the cane-sugar under different influences during the process of preparation.

The early fermentation of saccharine vegetable fluids, which have been expressed a phenomenon very common in the manufacture of sugar in the tropics, proves the action of the nitrogenous substances contained in these juices, for, as far as our present experience goes, they alone can produce those changes which we denominate fermentation.

The observation that after the continued boiling of a solution of sugar, only a part can be preserved as sugar fit for crystalization, points out heat as another agent, or influence.

There is no doubt that the influence of such agents diminishes the yield of the refiner; but I doubt whether a correct judgment has been formed of them, and without this, improvements in the manufacture of sugar are not possible.

To obtain this end experiments had to be made on a small scale. These I made by trying to submit solutions of sugar to the influence of the same agents to which the sugar in the juice, and during the whole process of preparation can be submitted.

In consequence of the insufficiency of chemical expedients to separate the newly formed kinds of sugar from the cane-sugar, and to determine their quantity, I found it impossible to ascertain the exact degree of decomposition which I observed under different influences. It is true that more recently the polarization of light has been applied to determine the quantity of the different kinds of sugar in a solution, and the degree of transformation of the sugar under different influences; I, however, did not apply this method, as it could only be of use to me in a few observations, but would be entirely inapplicable for the greater part. I moreover doubted the correctness of the re-

sults in these cases, for reasons to which I shall revert hereafter. The results of this method, as given in the works of Ventzke,* and Soubeiran,† I have, however, constantly compared with my own.

I.—Influence of atmospheric air upon a pure solution of Sugar, at a common temperature.

Sugar dissolved in pure distilled water can be preserved for weeks in closed vessels, without undergoing any changes; but if, on the contrary, we expose a solution of about 10° B., to the air in a tumbler, and protect it against dust, we find already after three days, traces of altered sugar, which increase daily. This fact had been observed before, and the change in the second case had been attributed to the organic substances contained in the air.

But whatever probabilities may favor this opinion, it would almost appear that the atmospheric air had an immediate share in bringing about these changes, for pure solutions of sugar, a large part of which is exposed to the air, change in a very short time. The following experiment will show this to be correct:

I filled a glass cylinder, open at the top and at the bottom, with broken glass, like an acidulating vessel for the quick vinegar process, and gradually dropped a pure solution of sugar, the purity of which I had before ascertained by the copper test, slowly, and in such manner, into it, that the air found unimpeded access. The liquid running out below, I continued to pour in at the top. The temperature of the surrounding air was 15° R. After six hours labor I found already altered sugar, for, on mixing with it sulphate of copper and alkali oxidule, (protoxide of copper) was separated. This change increased rapidly, and after 36 hours of operation, the decomposition had progressed so far, that, on evaporation under the air-pump, first, no crystallization was obtained, and after many trials, only a very sparing one. The liquid had remained colorless during these trials, but had become somewhat dimmed.

Whether the effect is produced by the influence of the oxygen of the atmospheric air, or by the organic substances, this experiment proves that considerable contact with the atmospheric air, can change a pure solution of sugar.

Influence of heat upon the pure solutions of Sugar in boiling.

A solution of sugar boiled for some time, or exposed to a temperature above boiling water heat, decomposes itself, as has been observed by many, and loses its power of crystallization. At the same time several new substances are formed, such as uncrystallized sugar, by some called sirop sugar, and noticed as a peculiar kind of sugar, formic and acetic acid, ulmic and ulmic acid.

These changes and transformations, under the influence of water and of heat, progress very slowly. To obtain a distinct view of the changes of a solution of sugar in boiling, a continued action of several hours is requisite. Many experiments made on a large scale, almost

* See Journal für Pr. Chemie, vol. xxv, p. 65, and vol. xxviii, p. 101.

† See Journal für Pr. Chemie, vol. xxvii, p. 281.

made me doubt the pretty generally received opinion, that the greatest part of the molasses obtained in the preparation of sugar, is sugar destroyed by heat. The previous experiments, where sugar solutions had been boiled for twenty-four hours and more, could not be considered as a practical standard; I therefore made the following experiments several times:

A solution of pure sugar of 25° B., I boiled in an open bowl at one trial for 1 hour, at another for 1½ hour, and at a third for 2 hours, and in such a manner that the evaporated water was not replaced until the temperature of the boiling mass had reached 110°—112°C. Even after two hours boiling in this manner, the mass remained colorless; left under the air-pump for crystallization it proved very copious. The liquid, after having been separated from the crystals for some time, formed a solid mass; but decomposition had taken place notwithstanding, for the test by copper showed traces of uncrystallized sugar, and when heated with lime-water the liquid changed to a yellow color. This experiment, repeated frequently, always produced the same result. When the solution of sugar is boiled in an alembic, the sugar undergoes a greater change than in the bowl; the time that the sugar is under the influence of heat being the same. It is difficult to account for this, for we might more readily suppose, that, as the air finds freer access to the bowl than to the alembic, the contrary would be the case. Perhaps this difference of behaviour, when boiling in the alembic, is caused by the flowing back of the water of condensation, which itself aids in the decomposition of the sugar through formic acid, which cannot be known by any test.

This may be the cause that Soubeiran, in his experiments, after the effect of a boiling heat of two or three hours, discovered considerable decomposition. In boiling sugar for a longer time, it becomes evident that the decomposition, under a more protracted influence, proceeds more rapidly than in the beginning of the experiment, because the products formed by the first action, aid in the decomposition of the sugar, and the more of these there are formed, the more will the transformation be accelerated.

According to Soubeiran, a solution of sugar decomposed by boiling, reacts strongly acid, and, in this case, the acceleration of the process of decomposition can easily be explained. I have not been able to ascertain whether a solution of sugar, which had been boiled for a long time in an open bowl, reacted as an acid upon litmus paper, yet there are in this liquid, acid products, which, as soon as alkalies are introduced, immediately destroy the alkaline reaction. Mixed with calcareous earths, we obtain partly indissoluble compounds. The formation of volatile and *non-volatile* acid products is incontrovertible, and from this we may deduce, that fruit and grape sugar must be formed in the same manner as when acids act upon cane sugar. The opinion that a peculiar kind of sugar is produced by the decomposition of cane sugar, appears to me, therefore, very hazardous. Ventzke* calls this sugar sirop sugar, and mentions, as its peculiar

* See Journ. für pr. Chemie., vol. xxv, 2nd series, p. 75.

quality, that it does not polarize the light. If we compare the phenomena, which accompany the transformation of sugar during ebullition, with the effects of diluted acids, we shall find considerable analogy, for in both acid products are the result. We may also take it for granted, that as soon as acid products have been formed, they exert their influence in such a manner as to generate fruit and grape sugar, and other productions. The perfect neutrality of the mass of sugar, examined by Ventzke, may, therefore, be accounted for on the principle, that grape sugar and fruit sugar existed in such proportions as mutually to destroy their power of polarization. A separation, or isolation, of these two kinds of sugar has hitherto been found impossible, by crystalization it would scarcely be possible to separate them.

To observe the influence of atmospheric air upon a boiling solution of sugar, a solution of 15° R., was boiled in an alembic, and a continued stream of atmospheric air guided through the boiling liquor, by means of a forcing pump (aspirans.) The influence of the air could not be mistaken here, for in less than one hour and a half the saccharine fluid had become considerably darker. The test by copper indicated a considerable decomposition, and the crystalization of the sugar, under the air-pump, was more difficult, leaving behind a darker colored sirop, than in those experiments where the boiling solution of sugar had not been similarly exposed to the air, for, in boiling in the open air, the generated steam prevents the contact with the air.

These experiments prove that the action of the heat in boiling solutions of sugar on a large scale, under the same circumstances, and during the period of ebullition, produces no observable effect when the solution is pure; but that the action of the oxygen of the air aids materially in effecting a transformation in the cane sugar.

Behaviour of the solutions of Sugar under the influence of Alkalies.

That cane sugar combines with alkalies, that from this combination it can be separated again by acids, without any alteration in its form, is known.

In the manufacture of sugar the combination with lime is of great importance; although it has often been demonstrated that lime stands in the same relation to sugar as all the other alkalies, yet the general opinion that large quantities of lime added to the saccharine vegetable juice destroys the sugar, is still prevalent among a large number of sugar refiners. To ascertain this point, and, at the same time, to obtain a knowledge of the behaviour of alkaline solutions of sugar under the influence of different agents, the following experiments were made:—

I prepared sugar lime, by digesting a solution of sugar with caustic lime, at a common temperature, and, after filtering it, I obtained a liquid saturated with lime, and as clear as water; of this I made use in all the subsequent experiments.

When this solution of sugar lime was mixed with carbonic acid, heated to a boiling heat, to drive off the excess of carbonic acid, and the liquid was separated, by filtration, from the carbonate of lime,

which had been formed, I obtained, after evaporation under the air-pump, a sugar perfectly pure, which, when dissolved, and the test of copper applied, did not show a sign of decomposition. Another part of this solution of sugar lime I boiled for two hours constantly over a free fire, always supplying the evaporated water; after which time I used carbonic acid in the decomposition, and the sugar made its appearance as in the foregoing experiments. One part of the solution of sugar lime I reduced by evaporation in a china bowl over the lamp, keeping it constantly boiling; the temperature rose to 120° C., (248° Fahr.) As the mass at this point became so thick, that I could not stir it, it was partially burnt, and the smell indicated the products which sugar forms when distilled dry with alkalies; after cooling, the whole mass was hard, so that it could be reduced to a powder. I separated the white pieces from those which had become brown, and had suffered by decomposition; the former dissolved in water without any residuum, and when decomposed with carbonic acid, did not present the least appearance of sugar incapable of crystallization.

These two results agree with the results of Soubeiran, according to which, sugar combined with alkalies resists the effects of heat better than the pure solution of sugar.

When a concentrated solution of sugar lime is for some time exposed to the air, the sugar may also be separated unchanged; but hereby a peculiar phenomenon is observed. The mass gradually attracts carbonic acid from the air, without carbonate of lime being separated as a precipitate; at last the mass becomes transparent like a jelly, and under the air-pump assumes the appearance of a transparent gummy substance. On attempting to dissolve this mass in water, large quantities of carbonate of lime are separated; the same occurs when the moist, jelly-like mass is diluted, or heated, with water.

That a solution of sugar will decompose carbonate of lime, is a known fact, but these quantities are so small, that they cannot be compared with those found in this case. Whenever I tried to dissolve newly precipitated carbonate of lime in concentrated, or diluted, solutions of sugar, or of sugar lime, I always found that only a small portion of the fluid had been absorbed; when I introduced carbonic acid into a solution of sugar lime, a precipitate of carbonate of lime would form immediately.

Why, in the above mentioned case, when the absorption of carbonic acid proceeded very slowly, no carbonate of lime was separated, I am not able to explain; but the phenomenon is interesting enough to be examined more carefully.

Concentrated, or diluted, solutions of sugar lime, which have been a long time exposed to the air, generally become somewhat darker, but even when they assumed the color of white wine, I could never discover decomposed sugar. The color is undoubtedly produced by organic substances, which, introduced from without, have been decomposed by calcareous earths.

Effect of neutral Salts upon the pure solutions of Sugar.

When alkaline chlorides, neutral alkalies, alkaline sulphates, and

alkaline carbonates were brought in contact with solutions of sugar, no other phenomena appeared than those which are observed in pure solutions of sugar under different influences.

The salts, however, interfere with the crystalization of cane sugar, particularly chlorides, and it appears as if they entered into actual combinations with the sugar. Péligot pretends to have obtained a crystalized compound of common salt and of cane sugar, other chemists have not succeeded with this experiment. Mitscherlich does not admit of a combination of common salt with sugar. I have not attempted to produce such a compound, but have limited myself to discover how far these salts are injurious to the crystalization of sugar.

In a solution of sugar to which I added two per cent. in weight of common salt in *one* experiment, and, in another, the same quantity of chloride of calcium, I could, by no means, produce any crystalization. When the mass is dissolved in water, and treated cold with much bone-black it crystalizes again, but it then only contains very small quantities of these salts. Alkaline carbonates have the same effect. Saline sulphates and carbonates partially crystalize from a solution of sugar, to which they are added in considerable quantities; a portion of them, however, form a greasy mass with the sugar. When added in very small quantities, as much as two per cent., they injure the crystalization of the sugar, but not as much as the chloride.

Influence of substances containing Nitrogen upon a pure solution of Sugar.

According to our experience, the presence of nitrogeneous substances is an absolute condition to produce in the solution of sugar fermentation, either vinous, acetous, or mucous; no saccharine vegetable juice is deficient in this respect, for all are capable of fermentation under certain circumstances. This power of decomposing sugar by the so called fermentation, does not belong to any particular nitrogeneous substance; but it has been observed that animal, as well as vegetable, albumen, casein, gluten, and generally the substances containing protein, can exert the same influence.

Another change remains to be mentioned here, which cane sugar undergoes through nitrogenous substances, and which must be of interest in the present case. H. Rose,* namely, has found that under the influence of fermenting substances, cane sugar, before the commencement of vinous fermentation, is transformed into another kind of sugar, namely, grape sugar,† and that cane sugar is not capable of immediate fermentation. It is very probable that not only the vinous fermentation is preceded by this change, but that all the other similar transformations of the cane sugar, are, in the same manner, preceded by a transformation into a kind of sugar capable of direct fermentation.

The general conditions of fermentation are a temperature above the

* Poggend. Ann. of Phys. and Chem. vol. li, p. 293.

† According to Venzke, fruit sugar.

freezing point, to about 40° R. (122° Fahr.) and access of the atmospheric air to the substances which affect each other.*

Access of atmospheric air is not only a condition to produce vinous fermentation, but also to effect the so called mucous fermentation. Mucous fermentation is easily formed in the expressed juice of the sugar cane when the air has free access; when excluded, no change takes place.

This is the basis of Apert's method of preserving vegetable juices. Péligré received from Martinique, cane sugar in its original state; the fresh cane juice had been heated to a boiling heat, and put in bottles whilst hot—the bottles had then been waxed. When this juice is taken out of the bottles, a mucous fermentation soon takes place. A similar experiment has not yet been made with the juice of the beet. The conditions under which nitrogenous substances are capable of producing the spirituous, milky, or mucous, fermentations, have not yet been ascertained. Boutron and Frémy have made an important contribution to the knowledge of the circumstances under which the milky fermentation takes place, in a very interesting work.† This work was particularly interesting for me, as milk fermentation is one of those changes which the juice of the beet manifests most frequently.

In the beet root we find vegetable albumen, and a number of other substances containing nitrogen; of the latter it has not been ascertained whether they belong to the compounds containing protein, and if they are fit to effect changes like these. That cane juice and beet juice possess the qualities of fermentation, is a well known fact. The only thing to be ascertained is whether, among the nitrogenous substances, the quality of inducing a change belongs solely to the so called albumen.

Let us first examine the phenomena which appear in the juice of the beet. When exposed to the air, immediately after expression, it frequently turns mucous very soon; it undergoes the mucous as well as the spirituous fermentation. On examining this altered juice, we find lactic acid, mannite, a gummy mass, and sugar, which cannot be crystalized. The juice of the beet may be preserved for twelve hours and longer, without any material change, but when once the process of decomposition has commenced, it proceeds rapidly; the smallest part of fermenting beet juice mixed with fresh beet juice, induces a change in a few hours. The juice of beet from which, by boiling, a considerable part of the nitrogenous substances, have been removed, manifest almost the same qualities as fresh beet juice; when exposed to the air it undergoes mucous fermentation, when the juice contains much or little free alkali. When the alkalinity of the juice has been diminished by acids, sometimes a spirituous fermentation takes place; but if we take the juice, although containing alkali, and moisten with it bone-black, press this mass into a glass, and keep it in a favorable temperature, a short time will suffice to produce spirituous fermentation, but no other.

I attempted to observe these phenomena on a small scale, by means

* Berzelius' Chemistry, vol. viii.

† *Ann. de Chim.*, Juillet, 1841, p. 257.

of the two nitrogenous substances, which I prepared from the precipitates of the beet juice with lime. By bringing a solution of sugar into contact with the calcareous substance, the liquid generally became weak, sour, and somewhat mucous, after a few days. Acid lactæ, and a gummy substance, which could be precipitated by spirits of wine, had formed; mannite I could not discover in these experiments. The substance insoluble in water, the albumen of the beet, brought in contact with a solution of sugar, induced similar changes, but not until after a greater lapse of time. The products were the same, a part of the albumen, before insoluble, was soluble, and could be precipitated by tannin. When the sugar solution was made weak by alkaline, and brought into contact with these substances, the alkalinity disappeared after a while, and the decomposition became the same as before. When I made the solution of sugar strongly alkaline, no change was observable for a length of time. In all these cases I observed that the cane sugar changed into another kind of sugar, and this before any signs of fermentation appeared. This change was very evident when I brought a solution of sugar of 10° R., to which I had added some of the calcareous substances, into free contact with the air, by means of a cylinder filled with glass, as before described. After a few hours all the cane sugar seemed to be transformed into another kind of sugar, without indicating the formation of any other products. Continuing this process for a sufficient time, the liquid at last became slimy, but not sour. In this case, the substances containing nitrogen, seem to operate in the same manner as in the formation of vinegar from wine. Acids, and principally mineral acids, can prevent the fermentation under these circumstances. By heating a solution of sugar, which contains nitrogenous substances, to boiling, or by boiling it for a long time, it does not lose its fermenting properties, as I have stated before: clarified beet juice ferments very easily. Beet juice which had been evaporated to 25° R., and had, therefore, been exposed for a long time to the action of the heat, changed completely when left alone in a bottle for some considerable time. Carbonic acid was generated, and forced the cork out of the bottle; after a fortnight the fermentation ceased, and it afterwards appeared, on examination, that neither spirits of wine, nor acids of any kind, had formed. The product was principally mannite, and a gummy mass which could be precipitated by spirits of wine in the watery solutions.

When bad cane sugar from the colonies is dissolved in water, and left to stand in a favorable temperature, it produces a phenomenon quite similar to that mentioned above, only that in this liquid I could find no mannite, undoubtedly because too much other sugar prevented its separation.

All these phenomena are the results of the influence of nitrogenous substances; wherever similar phenomena appear, such substances will be discovered. Substances containing nitrogen may produce effects different from those mentioned just now at a higher temperature, that is to say, in contact with boiling solutions of sugar, or at temperatures a little above the boiling point of water.

It is a known fact that when a concentrated solution of raw sugar

and one of loaf sugar is left for some time in a temperature of 110° , the raw sugar solution changes much more than that of refined sugar. The supposition that in this case a direct transformation is effected in the sugar, by the nitrogenous materials contained in the mass, is not improbable.

This opinion obtains confirmation from the following experiment: Take a simple solution of sugar, and a solution of the same sugar clarified with blood; boil both for the same length of time, and the clarified solution will soon become discolored, whilst the simple solution remains colorless. In every clarified solution of the sugar refiner, even where the purest sugar has been used, we find substances containing nitrogen, which can neither be precipitated through tannin, nor this reagent (the blood.) It is possible that the clarified solution may be free from these substances, when very fresh blood is used; this remains to be tried, for it is certain that the older, and the more impure the blood, and the more albumen is changed by putrefaction, or whatever else this decomposition may be called, the greater will be the quantity of nitrogenous matter contained in the clarified solution; nor is it unlikely that the albumen of the blood, during the process of clarifying, is, by the influence of the heat, so changed, that it either coagulates no more, or when coagulated, dissolves again.*

I obtained the same results when I mixed and boiled a pure solution of sugar with the calcareous substances, frequently alluded to. The solution became of a darker color, and the test by copper indicated the formation of another kind of sugar. In this case the substance containing nitrogen had evidently changed, for, on continuing the boiling for some time, lime water, indeed, produced a precipitate, but only a trifling one, whilst nitrate of mercury produced a very abundant precipitate; before boiling, the substance could be perfectly precipitated with lime.

The products which are formed in this decomposition of nitrogenous substances, I have examined no further. I should suppose that during this change, ammonia is generated and emitted, whilst the remainder of the elements combine to form acid products, and effect the same changes on the sugar as all acid substances do. The brown color of sirop is mainly attributable to such products of decomposition.

The behaviour of substances containing nitrogen, during ebullition, and at higher temperatures, as in concentrated solutions of sugar, has been but little examined as far as I know. Only a few substances, lime and albumen, have been observed under similar circumstances, and have been found to change. In these experiments, the substances came only in contact with water, and the temperature was consequently not much above 100°C. ; at higher temperatures the behaviour will be probably somewhat different, because, in general, some of these bodies are decomposed with more or less facility, accordingly as their elements are grouped more or less densely.

From what has been said before, we may conclude that the nitrogenous substances of the beet, and probably those of the sugar cane, can exercise different influences every where at the common tem-

* See Berzelius *Lernbrech der Chemie*, vol. viii, page 792.

perature, when these juices are left to themselves, and exposed to the air; and further, by heat during the process of boiling.

To be Continued.

FOR THE JOURNAL OF THE FRANKLIN INSTITUTE.

On the Strength of Cylindrical Boilers. By THOS. W. BAKEWELL.

It is not my intention to prolong this discussion beyond a few remarks, on an unexpected denial by "E," in the October number of the Journal, of a proposition stated in my reply, (vol. vi, page 210.)

The estimate of the force to rupture, by the theory I advocate, is fair matter of dispute; but the proposition, above referred to, is the legitimate product of the received doctrine. In calculating the parting force, by the received theory, it is necessary either to suppose that the vessel containing the steam, possesses sufficient stiffness and strength to be unalterable in its shape, *independently* of any form which may give it this quality; or, what is the real state of the case, and the source of error, to overlook this circumstance altogether. Therefore, the transverse section, or diameter, determines the parting force, without regard to the form of the ends of the vessel on either side said diameter—that the direct force of the steam, perpendicular to the diameter, and such part only of the oblique forces as may be resolved into direct, are operative in parting the vessel at the diameter—and that the remaining forces derived from the oblique, being resolved into a direction parallel with the diameter, need not be taken into the estimate. The proposition made by me, presents the figure, or segment, of a boiler, A, B, D, C, attached at A and D, to a solid body, C. The substance of my averment, was, that by the received theory, the force to part at B, was half that exerted at A or D. "E." admits that the diameter governs at A and D, and that the whole force is sustained, one-half each, by A and D; but denies the applicability of the rule to the diameter, B, C, of the figure; or that the *half only* of the amount of force on A, D, is borne jointly and equally by B and C. Draw the semi-circle, as shown, on B, C, for the termination of *that* end of the figure, and let the line, B, C, be a tie bolt, considered sufficient to preserve the shape.

Can this change, in the form of one of the ends of the figure, vary the parting force by the steam at B? but the semi-circles on B, C, and on A, D, are similar, and under like conditions.

If it be said, the tie bolt, to preserve the shape, and perpendicular to the considered direction of rupture, lessen the strain at B, then, indeed, do we approximate in opinion; but as this admission cannot be looked for from "E," I maintain that the proposition is incontrovertible,—viz., that B, sustains half, and only half, of the force on diameter, B, C, in like manner with A, D, as to their diameter. I wish it to be well noted, that the force to part at B, by the *received* and