

The Chemistry of Lime Salts in Sugar Beet Juices

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THE CHEMISTRY of lime salts in sugar beet juices presents, both from the practical and the theoretical point of view, many features of great interest.

We see in practice a complete range, starting from juices with practically no lime salts at all—giving no precipitate with ammonium oxalate solution—up to juices with several tenths of a p.c. of CaO. We see sugar industries—like the Swedish one—very careful about the slightest increase in lime salts—and on the other side—e.g. the Irish one—processing without great troubles juices extremely high in lime salts—with complete indifference to them.

If we try to formulate the more important practical experiences, concerning the behavior of lime salts, we can list them in the following order:

1. In second-carbonation juices there exists lime salts and (carbonate?) alkalinities simultaneously in concentrations far exceeding those ever found in water solutions. This fundamental fact has been formulated in a very clear way for the first time—as far as I know—by two Czech chemists, V. Sykora and J. Schiller in 1881.
2. The amount of lime salts is not inversely proportional to the alkalinities of juices. Sometimes even strongly alkaline juices contain great amounts of lime salts.
3. A high second-carbonation temperature sometimes increases, sometimes decreases the amount of lime salts.
4. The same contradictory observations have been made when boiling out unfiltered second-carbonation juices.
5. The addition of soda ash does not precipitate the equivalent amount of lime salts. The efficiency of precipitation varies very considerably from juice to juice.
6. Soda ash—though decreasing the lime salts in second-carbonation juice—increases sometimes the rapidity of scaling in the evaporators—so that many practical sugar men prefer to process juices high in lime salts—rather than using soda ash.
7. The amount of scaling is not proportional to the amount of lime salts in second-carbonation juices. It seems that not all lime salt is “harmful.”
8. Evaporation thick juice does not always yield incrustations—though it ought to be a very strongly supersaturated solution of (at least) CaCO_3 .
9. The alkalinity (pH) of the thick juice is sometimes higher, sometimes lower than the alkalinity (pH) of the corresponding second-carbonation juice.

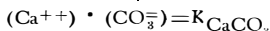
10. The formation of scales has been observed even before the evaporation, i.e., in the filter clothes of second-carbonation filters etc., though the optimal second-carbonation alkalinities have been maintained correctly.

11. Scales formed, say in the first part of the campaign, have been seen redissolving again in the further course of the processing season, and this even with juices very rich in lime salts.

It is rather interesting to see how these contradictory, seemingly unrelated facts can be made to fit beautifully in one single and coherent picture of the behavior of lime salts—if we try to understand them, in other words to formulate them in a somewhat theoretical way.

This theory is a very primitive one.

A. We are eliminating the Ca^{++} from our juices in the form of CaCO_3 , which leads to the fundamental equation



The product of the concentrations of the Ca^{++} and the $\text{CO}_3^{=}$ in a certain saturated CaCO_3 solution has a constant value, called the solubility product of CaCO_3 .

Let us see what this simple equation can teach us.

In figure 1 are reproduced two solubility (ionic) products (Ca^{++}) and ($\text{CO}_3^{=}$), one of which has the value $K=1$, the other one $K=16$. It is now important to remember that when we know the composition (eg) (Ca^{++}) and ($\text{CO}_3^{=}$) of one sample of a—say second-carbonation juice—we are able to trace the whole corresponding curve, for which (Ca^{++}) ($\text{CO}_3^{=}$) has the same value.

These curves allow us to follow the deliming effect of an addition of soda ash. Say our juice has the composition of point 1 at curve $K=1$ and we add an amount of soda ash equivalent to 1 part of $\text{CO}_3^{=}$. A simple geometric construction allows us to find point 2 giving the composition of juice 1 after soda-ash treatment. The vertical line in 2 gives the deliming which is very marked in this case. Other similar cases are marked by points 3, 4 and 5, 6.

We see clearly that—in order that K remains constant—one part of the soda ash added must be utilized to increase the $\text{CO}_3^{=}$ concentration and thus cannot react with the Ca^{++} —in other words the soda ash can never precipitate equivalent amounts of Ca^{++} .

The comparison of point 1 and 3 tells us that—all other conditions equal—the less lime salts a juice contains, the less effective is a certain addition of soda ash—and the comparison of points 1 and 5 shows that in different second-carbonation juices having the same concentration of lime salts (Ca^{++}), the deliming effect of a certain amount of soda ash is the smaller, the greater the K_{CaCO_3} of such juice.

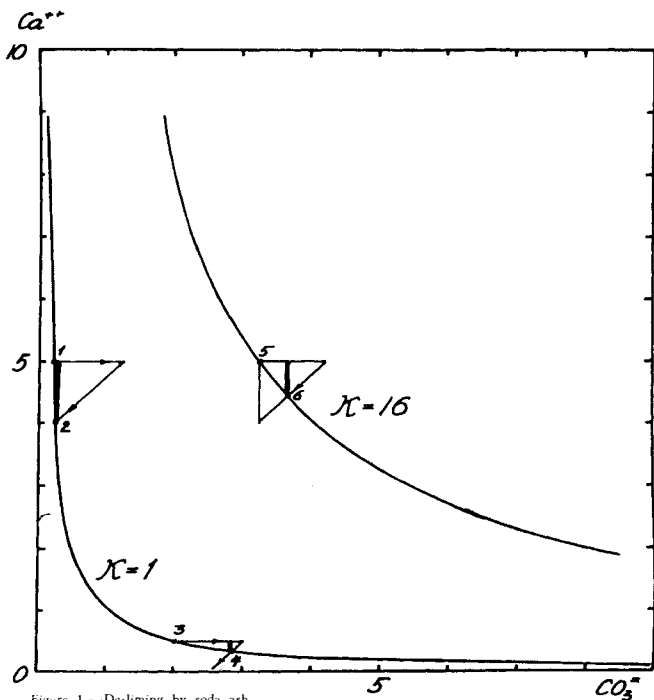


Figure 1.—De-liming by soda ash.

Thus the effect of soda ash depends on the position of the corresponding juice on its K -curve, 1 as against 3, and on the absolute value of K , 1 against 5. This gives a satisfactory explanation of No. 5 of our list.

But the decrease of Ca^{++} , due to soda ash, must not necessarily mean also a decrease in the amount of CaCO_3 , which could eventually form deposits. This is emphasized in figure 2. Juice 1 has twice as much lime salts as juice 2—the latter having been treated by soda ash. But the total amount of CaCO_3 which could crystallize out as such is given not by the content of Ca^{++} but by the much smaller amount of CO_3^{--} which is so to say the "limiting factor" in these two juices. This amount can be read at the CO_3^{--} axis and is marked by the end points of the vertical lines drawn from 1 and 2.

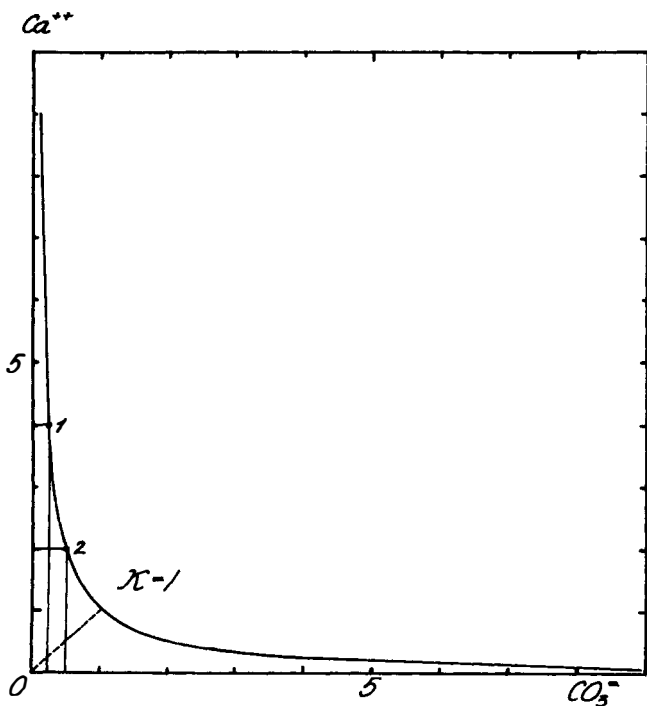


Figure 2.—“Paradox” of the soda ash treatment.

We see clearly that, by decreasing—by soda ash—the Ca^{++} of juice 1 to one half in juice 2 we have at the same time doubled the amount of CO_3^{--} in other words doubled the quantities of $CaCO_3$ in solution—and thus also increased the danger of scaling by $CaCO_3$. We called this rather unexpected effect the “paradox” of soda-ash treatment and it gives us a good explanation of No. 6 of our list of puzzling facts.

Both our curves give us also a simplified picture of the possible changes due to the evaporation of second-carbonation juices to thick juices (figure 3). If we abstract of all—the very many complications which actually take

place—we can consider what happens if the volume of second-carbonation juice is decreased to $\frac{1}{4}$ in the evaporation. In such case both Ca^{++} and CO_3^{--} increase 4 times and their product becomes $K=16$.

If we suppose further—in the first approximation—that the solubility of CaCO_3 in thick juice is the same as in the original thin juice (K thick juice=1), part of the CaCO_3 must crystallize out.

It is practical to subdivide the process in two steps—considering first the formation of a very supersaturated solution with $K=16$ and then the crystallization of CaCO_3 .

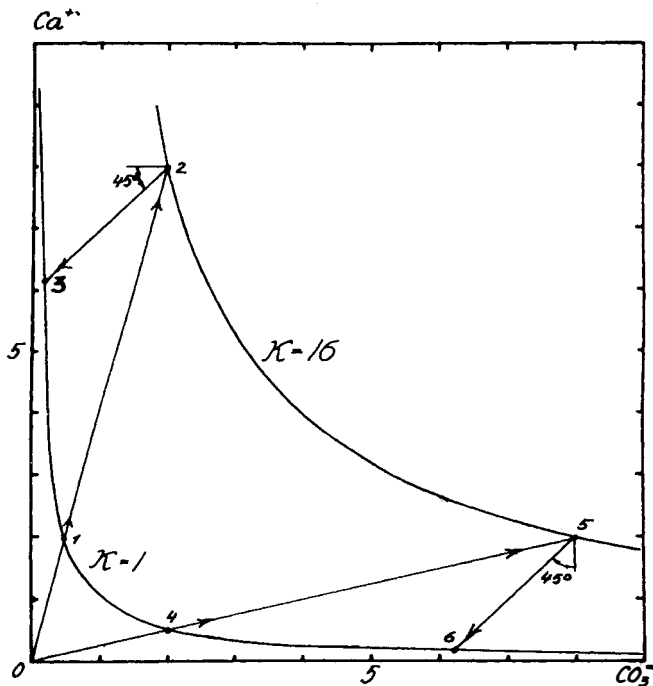


Figure 3.—Change in CO_3^{--} and Ca^{++} in the evaporation.

Figure 3 gives us both curves $K=1$ and $K=16$. We shall start evaporating the second-carbonation juice marked by the point 1. Its composition changes along the line 0-1-2, where Ca^{++} and $\text{CO}_3^{=}$ increase in the same proportion. The point 2 marks the composition of the strongly supersaturated thick juice ($K=16$).

If in the second phase of the process, CaCO_3 starts crystallizing, equivalent amounts of Ca^{++} and $\text{CO}_3^{=}$ disappear from the solution as solid CaCO_3 and the composition of the juice changes along the line 2-3, the point of intersection with curve $K=1$, representing the composition of the thick juice, just only saturated with CaCO_3 .

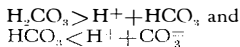
Points 4, 5, 6 are telling the same story of the second-carbonation juice of composition 4.

It is now very interesting to see first of all what happens with the alkalinity between thin and thick juice. We see that it has slightly decreased in the case of juice 1 and very markedly increased in juice 4. (A corresponding opposite change took place in the—volume—concentration of Ca^{++} .) This solves the mystery of contradiction No. 9 of our above list.

The difference in the Ca^{++} of 2 and 3, or 5 and 6 gives the amount of Ca^{++} crystallized out in the form of CaCO_3 . These differences plotted against the $\text{CO}_3^{=}$ contents of the corresponding original thin juices give curve Δ in figure 4. We see again the "paradox" of the decreasing danger of (CaCO_3) scale formation, as the content of lime salts in the thin juice increases—the most dangerous juice being the one having $(\text{CO}_3^{=}) = (\text{Ca}^{++})$.

There is still one point of great interest and practical importance, which can be easily guessed from figure 3 or 4, namely the influence of a decrease in $\text{CO}_3^{=}$. We see clearly that a slight loss in $\text{CO}_3^{=}$ during evaporation of juice 1 would shift 2 along a line, parallel to the $\text{CO}_3^{=}$ axis and at the same time lift 3 along the curve $K=1$ —up to a moment, when 2 and 3 would coincide in the $K=1$ curve. In such a case there would be no CaCO_3 in over-saturated solution and the thick juice would be a saturated solution of calcium carbonate. A further loss in $\text{CO}_3^{=}$ would give a thick juice under-saturated in CaCO_3 and thus capable of even dissolving CaCO_3 scales already formed! We see further that the absolute loss of $\text{CO}_3^{=}$ necessary is the smaller, the greater the amount of Ca^{++} in the thin juice. This explains No. 11 of our list.

B. The above mentioned possibility of a change in the $\text{CO}_3^{=}$ concentration brings us to the second theoretical point we must discuss. It is the dissociation of carbonic acid. We all know that it dissociates in two steps



with $\text{p}K_1=6.36$ and $\text{p}K_2=10.25$ at 25°C . A graphical extrapolation of the values for different temperatures gives approximately 6 and 10 for 85°C . (figure 5). We all know that—but we somehow forget all about it when discussing second-carbonation. We especially forget the tremendous importance of the pH on the degree of ionization—that is on the per-

centage of the total carbonic acid present, which exists in the $\text{CO}_3^{=}$ form and which is the only one taking part in our fundamental equation $(\text{Ca}^{++})(\text{CO}_3^{=}) = K_{\text{CaCO}_3}$.

A simple calculation shows, however, that between pH 8 and 9 the percentage $\text{CO}_3^{=}$ increases from 0.6 to 5.6 percent. A further rise of the pH to 10 increases the percentage $\text{CO}_3^{=}$ to 37 percent. Now the extreme pH of normal, healthy and correctly carbonated second-carbonation juices of my country are, according to our experiences 8.2 and 9.4, which (at 25°C) correspond to from 1 to 13 percent $\text{CO}_3^{=}$.

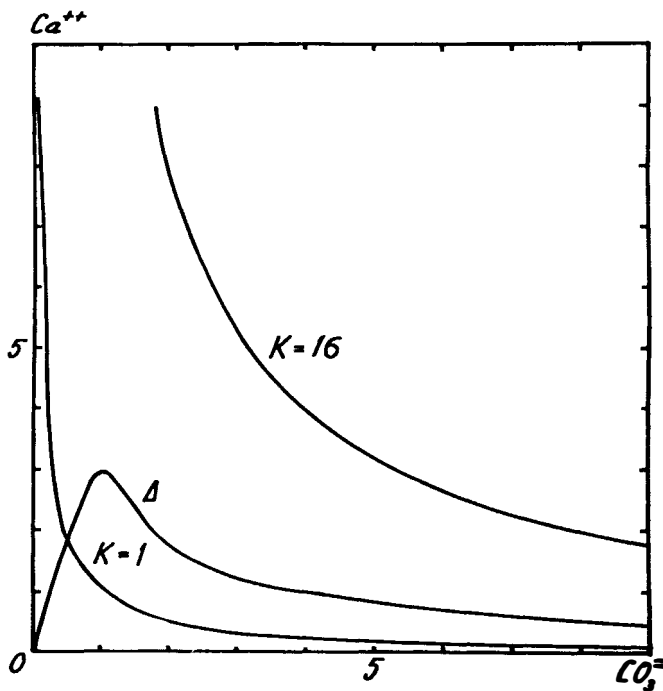


Figure 4. Amount of CaCO_3 ; (Δ) in supersaturated solution.

It is not without interest to compare these values with the total amount of carbonic acid present in the same juices. In our own determinations we found (expressed as CaO p. 100 ml) values between 5.2 and 70.3 mg. Now, if such quantities of carbonic acid were present in the form of Na_2CO_3 in pure water solutions, the corresponding pH can be easily calculated and would be from 10.6 to 11.2—thus far higher than those of our thin juices. In the water solution up to 90 percent of all the carbonic acid present exists in the $\text{CO}_3^{=}$ form, as compared with 13 percent in the juices! What is the reason of these low values in juices?

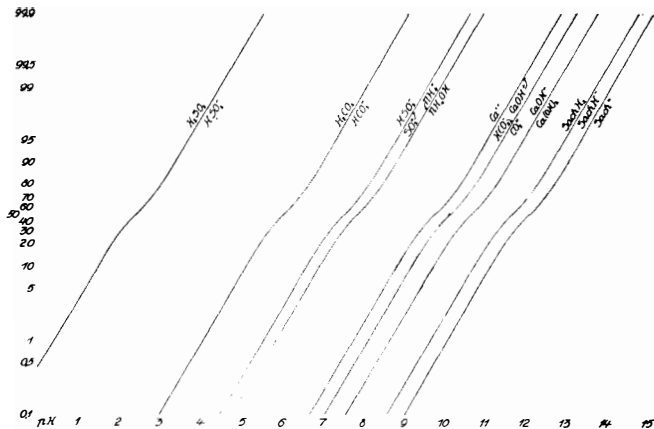


Figure 5. Ionization curves.

Here, the Na_2CO_3 or K_2CO_3 is not dissolved in pure water but in a solution of an acid—the sucrose, whose pK_1 of 12.6 at 25°C . is sufficiently close to the pK_2 of carbonic acid, to be able to depress considerably its dissociation—and thus render it still more difficult to “delime” our juices.

From the figure 6, reproduced from the very interesting article of the young Danish chemist H. Brueniche-Olsen (SUGAR, October 1947), follows, that in a sugar solution at 85°C . in the maximum about 25 percent $\text{CO}_3^{=}$ exist at a pH of 9.5. His pH values have been of course measured by the aid of a tungsten electrode.

In any case, this influence of sucrose on the ionization of carbonic acid explains away the puzzle No. 1—the coexistence of large quantities of lime salts and “carbonate” alkalinities in beet juices.

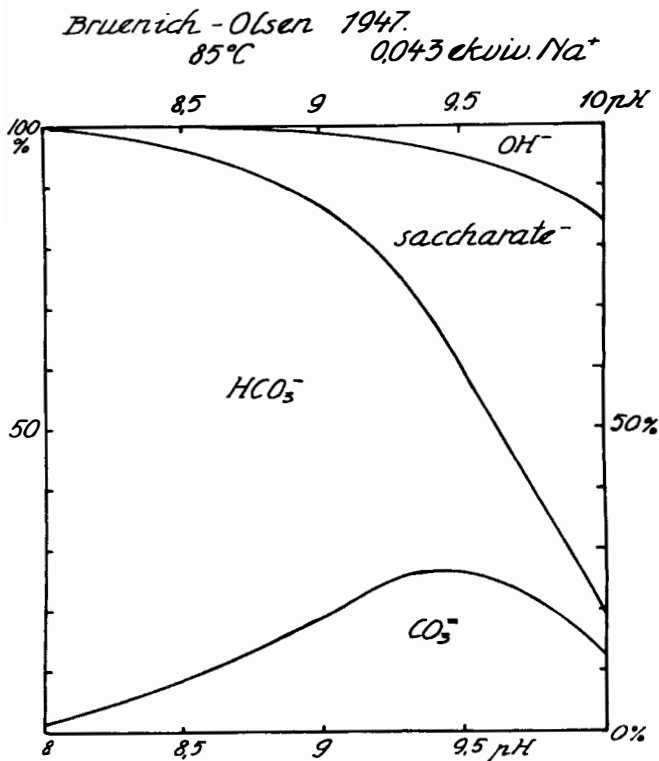


Figure 6. Ionic equilibria of Bruenich-Olsen.

C. It is time to consider now the ionization of the $\text{Ca}(\text{OH})_2$. This is a divalent base and the literature is giving its $\text{pK}_1=11.6$ and $\text{pK}_2=12.5$ at 25°C .—which by a rather uncertain extrapolation gives 9.7 and 10.6 at 80°C .

We see that $\text{Ca}(\text{OH})_2$ is a very weak base, whose pK overlap those of carbonic acid and sucrose (figure 5). This is the reason why there is little possibility for milk of lime to react in solution with sucrose—as can be

seen from figure 1, giving the ionization curves in Michaelis' form (percentage ionization) of the different ions which $\text{Ca}(\text{OH})_2$ resp. sucrose (considered as a divalent acid, $\text{pK}_1=12.6$, $\text{pK}_2=13.1$) can form. In order to ionize sucrose—we need big pH-es, at which however the ionization of $\text{Ca}(\text{OH})_2$ is but very low—and vice versa. The different intersection points (a, b, c, d) show the maximum amounts of the different cations (CaOH^+ , Ca^{++}) and anions (Sach H^- , Sach^-) which can co-exist. The highest value (c) is only about 21 percent—all the rest being "hydrolyzed." This is the explanation of one of the difficulties of a Steffen method—and also of the advantages of the barium process—where we utilize the much stronger base $\text{Ba}(\text{OH})_2$ with a pK_1 of 13.28, which is 1.6 higher than the pK_1 of $\text{Ca}(\text{OH})_2$.

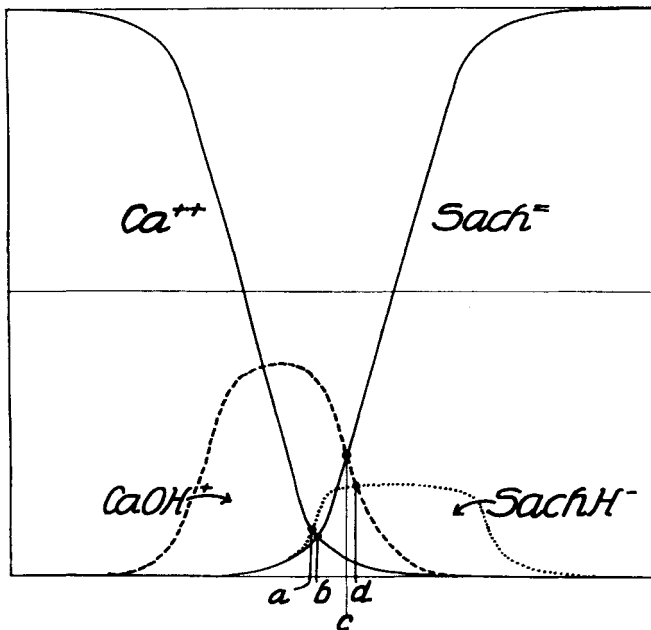
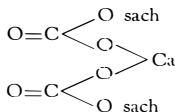


Figure 7.—Reactions of $\text{Ca}(\text{OH})_2$ with sucrose.

The possible reactions of carbonic acid ($\text{CO}_3^{=}$ and HCO_3^-) with milk of lime (CaOH^+ , and Ca^{++}) can be guessed in a similar way from figure 8. We see that about 42 percent of CaCO_3 can exist in solution unhydrolyzed—and nearly 98 percent of $\text{Ca}(\text{HCO}_3)_2$, H_2CO_3 being a stronger acid than HCO_3^- .

The reactions are still more complicated when considering all the three components, namely, carbonic acid, sucrose and milk of lime simultaneously—say in neutralizing a $\text{Ca}(\text{OH})_2$ —sucrose solution with carbonic acid. The school of Bjerrum and Faurholt have been able to show that in such a case—at least at lower temperatures—the primary products are alkyl-carbonates possibly of the type



which in a secondary, rather slow reaction decompose into free sucrose and CaCO_3 .

This is one of the reasons why limpid sugar-lime solutions can be treated with CO_2 at low temperatures without giving the slightest precipitate; we were able to keep them for hours, absolutely brilliant and limpid.

D. The conditions are getting still more complex if we take in consideration the presence of other substances (ions) than sucrose, carbonic acid and lime.

As we are mostly interested in lime salts—let us start with the anions, which must necessarily accompany any Ca^{++} of lime salts.

It is very interesting that already 20 years ago, in 1928, a Dutchman, van der Heide, in a very important paper (published in *Chemisch Weekblad*), which however remained completely unobserved, was able to show the importance of the pK of the acids forming lime salts. Figure 9 reproduces a part of his curves. We see clearly that the weaker the acids (the higher their pK) the smaller amount of Ca^{++} remains in solution and the higher the corresponding “optimal” pH of the second carbonation.

We can resume, in a crude way, the results of van der Heide in saying, that carbonic acid partly liberates the “free acids,” forming the lime salts. These depress the pH the more, the stronger the acid present.

We become thus aware that it is not allowed to consider only our fundamental equation $(\text{Ca}^{++}) (\text{CO}_3^{=}) = K_{\text{CaCO}_3}$ —but as we have already learned from the influence of the sucrose on the ionization of carbonic-acid—that we must respect the interplay of all the ions present in the juices.

The second non-sugars which we can take in consideration are the aminoacids (and ammonia).

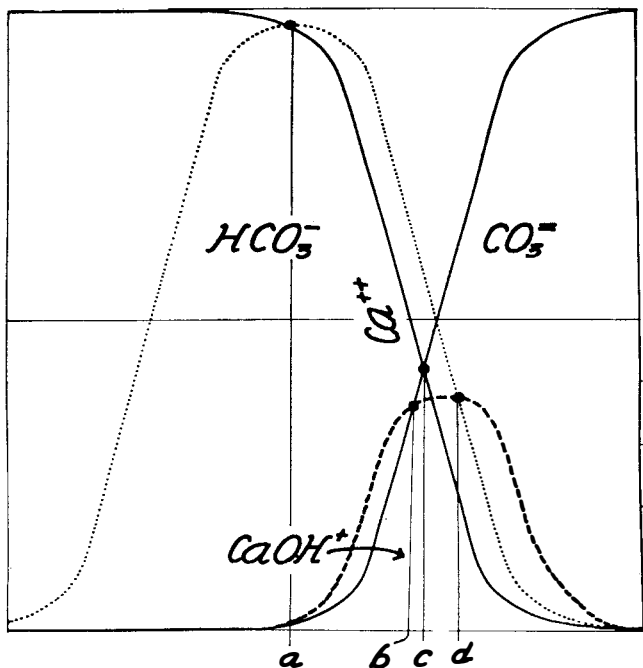
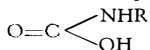


Figure 8. Reactions of $\text{Ca}(\text{OH})_2$ with H_2CO_3 .

Faurholt has extensively studied the reactions, velocities and equilibria between carbonic acid and ammonia resp. aminoacids in forming carbaminates of the type



The papers of Faurholt present a fascinating subject which however is mostly outside our present aim. But we must point out that this type of reaction can account for a part of the "non carbonate" CO_2 bound in the juices (see also the papers of Majer).

We are indebted to Siegfried for a thorough study of the solubilities of the Ca-carbaminates of amino acids. It is still an unsettled question whether these badly soluble salts can be present in the juices under condi-

tions of our carbonations and can account for any NH_2 —nitrogen being eliminated in the usual juice purification—or increase the amount of lime salts of our second-carbonation juices.

There is a certain evidence that protein substances, or their destruction products, if not properly eliminated are able to increase the solubility of CaCO_3 —either by some form of the Siegfried reaction—or by diminishing the activity of CaCO_3 .

Figure 10 shows the possible interreactions of $\text{Ca}(\text{OH})_2$ with the manifold ionized forms of a protein (the curves correspond to egg-albumin, whose dissociation constants have been determined by Ettisch and Schulze).

We can easily imagine how complicated the diagram would become if we were to include the curves for sucrose, carbonic acid and the different possible carbamids!

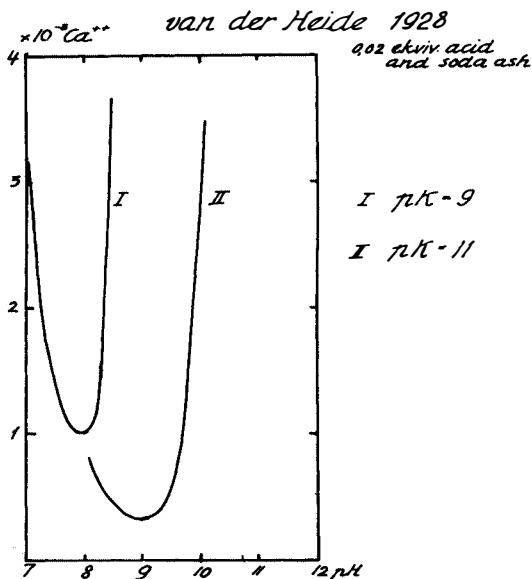
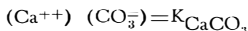


Figure 9.—Influence of the strength of acids forming lime salts on deliming.

E. We have just mentioned activities. In reality—even our fundamental equation



deals exclusively with activities and not concentrations. Thus, not the total amount of—say—lime, determined by soap solution in our juices, but only the active concentration of the Ca^{++} , the $p\text{Ca}$, takes part in the above equation.

The activity of the calcium ion is extremely important in the human physiology, but—up to the present time—no rapid and sufficiently precise method for the determination of $p\text{Ca}$ has been found. We are still very far away from anything which would resemble even an old fashioned hydrogen electrode for the determination of $p\text{H}$ —not to talk of the splendid glass electrodes.

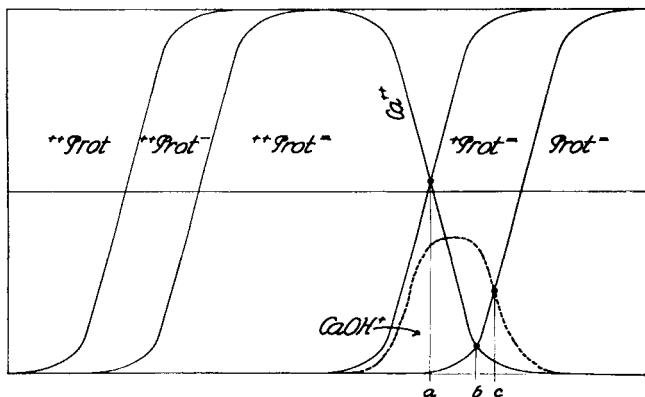


Figure 10.—Reactions of $\text{Ca}(\text{OH})_2$ with avaluamin.

But even the results arrived with the aid of the crude methods used at present enable us to draw some very important conclusions regarding our problem of lime salts.

The Danish chemist Kilde, working in the laboratory of Bjerrum, was able to show that in a 17 percent sugar solution, containing 0.3 to 0.5 percent CaO , only about 2 to 8 percent of the total amount of lime exists as Ca^{++} .

The British electrochemist Davies proved that lime salts of $\alpha\text{-OH}$ or $\alpha\text{-NH}_2$ acids give off only some few (2.4) percent Ca^{++} . The effect of citric acid on the ionization of Ca is well known.

Both Davies and Kilde have independently been able to prove the existence of complex Ca-ions of the general formula $(Ca An)^+$.

Chelated Ca salts of α -NH₂ acids discovered by Davies, would be another form of undissociated lime salts—all of which of course merely increase the total amount of Ca in our juices—without taking part in the fundamental equation of the solubility product of CaCO₃.

How important and manifold are even reactions between Ca⁺⁺ and proteins can be guessed by the recent monography of 28 pages by David M. Greenberg of the University of California Medical School.

Two of my collaborators, F. Cuta and M. Sevela, using Harnapp's electrode, tried to determine—for the first time in the beet sugar industry—the pCa of sugar beet juices—and found, from thin juices to molasses, values ranging from pCa=10⁻⁴ to 10⁻⁹—thus extremely low values, though these products contained several tenths of milligrams CaO/100 ml.

This again helps to explain the puzzle No. 1 of our above list—but itself creates a new problem—how to explain this low pCa and how to understand it.

F. But in processing our juices—and creating lime salts—we do neither use calcium ions nor carbonate ions. From the gaseous CO₂ of our carbonation gases there is a very long and complicated way to the CO₃⁼ we have been talking about. In order to see the complexity of the problem, it is however necessary to point out, that CO₂ first has to be absorbed and dissolved as a gas. Then it is hydrated to H₂CO₃—by reactions studied i.e. by Faurholz, 1924, in a paper of 70 pages. Vasátko and myself have just only touched the problem of the influence of sucrose and non-sugars on the velocity of CO₂ hydration. The whole field is still full of open problems.

We find the same state with CaO, which Kohlschütter considers to be a solid colloid, dissolving to a marked degree as a colloid, so that van Aken and later Kmunicek could ultrafilter limpid CaO-sucrose solutions through membranes. There is yet nothing known about the importance of the degree of dispersity of CaO on the effect of the juice purification, the formation of lime salts, etc., etc.

G. We have already mentioned the changes taking place during the evaporation. Figure 5 shows how great are the amounts of H₂CO₃ (and consequently of CO₂) in juices of normal pH. It is, therefore, quite natural that part of this CO₂ escapes with the vapours, thus decreasing the total amount of carbonic acid (which tends to decrease the CO₃⁼)—but at the same time increasing the pH (which tends to increase the CO₃⁼). This only adds to the complexity of the conditions.

H. Still more potent and difficult to master are the various destructive reactions (of sucrose, reducing sugars, amides, ammonium, etc.) which take place before, during and after the juice purification and give all raise to acid products—decreasing the pH and, or, increasing the amount of lime salts present.

I. But—when delimiting our juices with carbonic acid—we must filter off the precipitated CaCO_3 . Or—there is again a long and painful way to go, e.g., the formation of a new phase with all its difficulties—we know so well from our boiling pans, where we produce a solid phase of sucrose. There are many indications that CaCO_3 forms very easily supersaturated solutions in second-carbonation juices and Brueniche-Olsen stresses this point again very emphatically in his above mentioned paper. This explains point 10 of our list.

The above is but a selection of the more important problems connected with lime salts in sugar beet juices. Many more could be discussed. Sufficient, however, has been said to make it clear, that the true meaning of this paper is not so much to give information about the chemistry of lime salts in beet juices, but to show the importance of theory and of fundamental research in the sugar beet industry. The writer would be satisfied if the above rudimentary applications of a very elementary electro-chemistry would show how theory can deepen our understanding—and, therefore, our mastering of technical processes—as nothing is more practical than a good theory.