XIV. ELECTRICAL CONDUCTIVITY AS A MEASURE OF THE CONTENT OF ELECTROLYTES OF VEGETABLE SAPS.

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IN the course of some work involving a comparison of various methods of extracting saps, it has been found necessary to give attention to conductivity measurements as a means by which the content of electrolytes of samples of sap might be compared. A considerable amount of recent work in plant-physiology has been based on determinations of this nature in which it has been generally assumed that the conductivity of saps can be employed as a direct, though possibly somewhat approximate, measure of the content of electrolytes. It is clearly of importance that this assumption should not be made without adequate investigation, but hitherto no such investigation appears to have been carried out. On the other hand there are grave reasons for denying the validity of the proposition, even as a first and very rough approximation except under certain strictly limited conditions. Attention was first called to this point by an examination of the results of the conductivity measurements made by Dixon and Atkins [1913] on fruit juices. These were found to be uniformly low and the observers point out that this is the case even where acid fruits are in question, the juices of which are known to contain large quantities of organic acids. They explain their results as a consequence of the relatively slight dissociation of organic acids, but this explanation cannot be accepted as sufficient, as will be shown in detail below. It therefore became necessary to examine the matter further.

Since all fruits contain considerable quantities of sugars, it was thought possible that the presence of these in the juices might lower the conductivity and thus account for the discrepancies observed. This supposition was confirmed by comparative determinations of the conductivities of certain electrolytes (potassium chloride and citric acid) in aqueous solution and in solutions containing glucose, from which it was evident that the reduction of conductivity is considerable and must be of importance in the case of sugary saps.

It was subsequently found that the influence of non-electrolytes on the conductivity of aqueous solutions of various electrolytes had been worked out in detail by Arrhenius [1892] for a number of typical substances—electrolytes and non-electrolytes—and the object of the present paper is to discuss the bearing of the results thus obtained on the determination of conductivity in plant juices, especially in relation to the estimation of the content of electrolyte as carried out by Dixon and Atkins [1913].

Arrhenius found that for concentrations of non-electrolytes up to 10 per cent. (by volume) the conductivity of a solution may be expressed by the equation

$$C = C_0 \left(1 - \frac{ax}{2}\right)^2$$

where

C = conductivity of the solution containing x per cent. (by volume) of non-electrolyte;

C_0 = conductivity of an aqueous solution of the same electrolyte at the same concentration, and a = a constant.

The constant a varies with the nature of the non-electrolyte and of the conducting solution. It increases with the concentration of electrolyte but the variation is very small for highly dissociated substances. Arrhenius distinguishes the following groups of electrolytes. In each group the value of a is approximately constant for a given non-electrolyte.

Group 1. Strong univalent acids and alkalies.

Group 2. Salts giving univalent anions and cations.

Group 3. Salts giving univalent cations and bivalent anions.

Group 4. Salts giving univalent anions and bivalent cations.

Multivalent acids and weak univalent acids usually give still higher values of a and the same is true of salts which only undergo slight dissociation, *e.g.* HgCl_2 . It is to be noticed that if $\frac{a^2}{4}$ which is very small be neglected

$$ax = \frac{C_0 - C}{C_0}.$$

The decrease in conductivity is therefore proportional to the concentration of non-electrolyte.

It has been already remarked that the concentration of a highly dissociated electrolyte can be varied within wide limits without producing more than a slight variation in the value of a . It is therefore impossible to find a general explanation of the reduction of conductivity produced by the addition of non-electrolytes by assuming a change in the degree of dissociation and this conclusion is supported by other considerations. Arrhenius attributes the greater part of the reduction to the increase of viscosity produced by the replacement of water by non-electrolyte, and he shows that for any given non-electrolyte a may be expressed with fair accuracy as a linear function of its viscosity in 1 per cent. solution. There is, however, some divergence due to change in the degree of dissociation and in the case of slightly dissociated substances

this factor cannot be neglected. It is to be noticed that the constants of the equation connecting a with the viscosity of the solution vary with the nature of the non-electrolyte. It is, therefore, impossible to find a general formula expressing C_0 in terms of C —the measured conductivity—and the viscosity.

The following examples taken from Arrhenius' tables will give some idea of the values obtained for a .

Table I. *Values of $a \times 100$ for various non-electrolytes.*

Non-electrolyte	Group 1	Group 2
Methyl alcohol	1.62	1.75
Ethyl alcohol	1.88	2.34
Isopropyl alcohol	2.03	2.56
Ether	1.63	1.99
Acetone	1.56	1.62
Cane sugar	2.44	2.99

Table II. *Values of $a \times 100$ for electrolytes of various constitution.*

Electrolyte	Ethyl alcohol	Cane sugar
Group 1	...	1.88
„ 2	...	2.34
„ 3	...	2.51
„ 4	...	2.39
H ₂ SO ₄ N/4	...	2.55
H ₂ SO ₄ N/200	...	2.53
Oxalic acid N/8	...	2.61
„ „ N/100	2.10	2.81

These values represent the percentage decrease in conductivity in a 1 per cent. (by volume) solution of non-electrolyte. By dividing by the density of the non-electrolyte, a more convenient value, a , is obtained which represents the percentage decrease of conductivity in a solution containing 1 g. of non-electrolyte in 100 cc. Table III gives values of a .

Table III. *Values of $a \left(= \frac{100a}{d} \right)$ for electrolytes of various constitution.*

Electrolyte	Ethyl alcohol	Cane sugar
Group 1	...	2.38
„ 2	...	2.96
„ 3	...	3.18
„ 4	...	3.03
H ₂ SO ₄ N/4	...	3.23
H ₂ SO ₄ N/200	...	3.20
Oxalic acid N/8	...	3.30
„ „ N/100	2.66	1.77

d for ethyl alcohol = 0.79.

d for cane sugar = 1.59.

It is now possible to estimate the correction which must be made in solutions containing non-electrolytes in order to obtain the corresponding conductivities in aqueous solution from the observed conductivities. Arrhenius'

equation may be taken as accurate up to 10 per cent. (by volume) of non-electrolyte. At 20 per cent. the error in the ratio $\frac{C}{C_0}$ is 4 per cent. Therefore in the case of plant juices the reduction of conductivity may without serious error be taken as proportional to the content of non-electrolytes. For cane sugar solutions the value of α is approximately 2; and glucose produces a very similar effect; the conductivity of a solution containing 5 per cent. of sugar is therefore reduced by 10 per cent. and the factor for the correction of the measured conductivity is $\frac{100}{90} = 1.11$. Since, however, many saps contain sugars and other non-electrolytes in much greater concentration than 5 per cent. the correction in these cases may be very large. The magnitude of this effect appears to have been much underrated in various recent researches on the conductivities of vegetable saps even where it is not altogether ignored. The work of Dixon and Atkins is a case in point, and it is interesting to calculate the conductivities of aqueous solutions corresponding to the saps investigated by them in cases where an approximate estimate can be made of the nature and quantity of the non-electrolyte present. For this purpose the values of C may be taken from a table compiled by Atkins [1916, p. 157] from results obtained by him and Dixon. They are shown below in Table IV compared with the corresponding values of C_0 .

Table IV.

Fruit	Concentration of sugar assumed	$C \times 10^5$	$C_0 \times 10^5$
	%		
<i>Citrus aurantium</i>	9	208	254
<i>Citrus limonum</i>	2	345	359
<i>Lycopersicum esculentum</i>	4	457	497
<i>Pyrus malus</i>	12	161	212
<i>Vitis vinifera</i>	14.5	112	158

Vaccinium oxycoccus has been omitted, as no estimate of its sugar content could be obtained. The sugar content of the other fruit juices is taken in round numbers from Wehmer's *Pflanzenstoffe* and C_0 is calculated from the equation

$$C_0 = \frac{100C}{100-x}, \alpha \text{ being taken equal to 2.}$$

The sugar content of fruits is of course very variable, therefore no approximation to accuracy can be claimed for the above figures; they serve however to show the order of magnitude of the error which must be produced by the sugars present in the juices; this amounts in the case of grapes to 40 per cent. It must be remembered too that the sugars are not the only source of error; the effect of alcohols, esters, pectins, dextrans and the remaining non-electrolytes other than sugars which are present has been ignored in the above calculation. In some cases these must play an important part, and a further

examination of one or two of the foregoing results may throw light upon this point besides providing criteria by means of which one may judge certain conclusions which Dixon and Atkins have drawn from their observations.

These conclusions are as follows: (1) that the influence of organic salts and acids on the conductivity is small [1913, p. 439] and (2) that "even in acid fruits by far the larger porportion of the osmotic pressure is still due to non-electrolytes" [Atkins, 1916, p. 157].

These statements as they stand are obviously difficult of acceptance and in the case of (2) the underlying fallacy is evident. Dixon and Atkins have made without further enquiry an assumption which is expressed by Atkins as follows: "that by finding the freezing point of solutions of some standard substance, such as potassium chloride, which have conductivities equal to those of the plant juices under examination, and by subtracting these values from the freezing points of the saps as actually observed, it is possible to get a very approximate measurement of the proportion of the osmotic pressure due to non-electrolytes. The values thus obtained are probably somewhat too low owing to the increased viscosity of the sap occasioned by the sugars in solution" [Atkins, 1916, p. 149]. This is in effect to assume a rough proportionality between osmotic pressure and electrical conductivity for which no theoretical basis exists, osmotic pressure being determined by the joint concentration of molecules and ions while electrical conductivity is a function of the number and velocity of the ions alone. How far astray the assumption may lead can be shown by examining the values obtained by Dixon and Atkins for lemon juice. Lemon juice is stated by Wehmer to contain 5 to 10 per cent. of citric acid; therefore the lemon juice examined probably represented at least a normal solution (6.4 g. in 100 cc.), the freezing point of which has been found to be -0.72° whereas by Dixon and Atkins' method the depression of the freezing point due to all the electrolytes in lemon juice works out at 0.170° . Indeed since the value of Δ for lemon juice was found by Dixon and Atkins to be 1.089° , and that for the acid it contains exclusive of salts has been shown to be of the order 0.7 it is clear that the depression of freezing point due to non-electrolytes must be very small. The conclusion stated above must, therefore, be reversed in this case. In lemon juice only a very small part of the osmotic pressure can be due to non-electrolytes.

Only a small part of this error can be attributed to the lowering of the conductivity by viscosity; the error is the natural result of the assumption that equi-conducting solutions of such substances as citric acid and potassium chloride contain an equal number of molecules and ions. In the case of a mono- or di-basic organic acid the error would probably be greater still. Where salts are in question the matter may be somewhat improved, since the degree of dissociation is rather more comparable with that of potassium chloride, but large differences still remain, and added to these is the effect of widely

divergent ionic mobilities, for in this case there are no mobile hydrogen ions present to compensate for the slowly moving anions. There is therefore no theoretical justification for the assumption and as the basis of an empirical formula it is far too precarious to be of any value even in the most limited field.

The conclusion drawn by Dixon and Atkins that the influence of organic salts and acids on the conductivity is small is based on the low conductivities which they observed. It has been shown above that these low results are to some extent a consequence of the presence of non-electrolytes in the saps, but in highly acid saps another very important factor must also be allowed due weight. It is well known that the hydrogen ion concentration of an acid solution may be greatly lessened by the addition of a salt of the same acid. In the case of organic acids possessing heavy slowly moving anions the conductivity is very largely due to hydrogen ions and in consequence the conductivity of a mixture of salt and acid may be less than that of the acid alone, especially where acid salts are formed. Thus the conductivity of a decinormal solution of citric acid was found to be 183×10^{-5} at 25° ; that of a similar solution which also contained $N/50$ sodium citrate was found to be 172×10^{-5} , while $N/100$ sodium citrate reduced the conductivity to 142×10^{-5} .¹

In these solutions where the principal electrolyte is an organic acid and where the degree of dissociation has been reduced by the presence of salts the action of non-electrolytes upon the conductivity becomes less marked and the value of α may fall very considerably below 2. The value of C_0 as calculated above will then be too high. The *joint* influence of organic salts and acids on the conductivity may thus under these conditions become relatively small and the assumption made by Dixon and Atkins be correct; but even where salts exert their maximum effect in reducing conductivity, the measured conductivity will still be very considerably below that of a corresponding aqueous solution if any considerable quantity of non-electrolyte is present.

It must also be observed that the values of α given by Arrhenius were in most cases determined for highly dilute solutions. These values tend to rise as the concentration of the electrolyte is increased, especially where, as for organic acids, the degree of dissociation of the electrolyte is largely reduced by increased concentration. This is an effect apart from and opposite to that produced by salts. Thus it will be seen from Table III that the effect of ethyl alcohol on the conductivity of oxalic acid is increased 24 per cent. when the concentration of the acid rises from $N/100$ to $N/8$. In order to ascertain the value to which α rises in highly concentrated solution, observations have been

¹ Since writing the above attention has been directed to two papers which bear upon this point. Haas [1917] gives measurements of actual and total acidity for a number of plant juices. Hempel [1917] examines the buffer effects produced by salts in the saps of various plants and the relation of P_H to titration in lemon juice.

made of the reduction of conductivity produced in solutions of normal citric acid by the addition of cane sugar and ethyl alcohol respectively. The solutions were made from ordinary commercial citric acid, equal volumes of 2*N* solution being diluted to normal. The results obtained are shown below.

Table V. *The effect on conductivity of additions of cane sugar and ethyl alcohol to normal solutions of citric acid.*

					Reduction of conductivity	
					$\times 10^5$	α
Aqueous solution ...	...	...	...	$C \times 10^5$ 553	—	—
Solution containing 2 % cane sugar	...			529	24	2.12
Solution containing 2.4 % ethyl alcohol...				497	56	4.21

The effect of alcohol on normal citric acid is thus nearly double that of cane sugar. Higher alcohols and esters appear to act in a similar manner and these may be of importance in reducing conductivity of the more acid fruit juices, but little is known as to the amount in which such substances are present in fruits.

There can be no doubt that the low conductivities which have been observed in fruit juices are due to two principal causes:

- (1) The action of non-electrolytes.
- (2) The mutual action of salts and acids in repressing dissociation.

Which factor will exert most influence must depend upon the nature and quantity of the acid present, the proportion of acid to salt and the concentration of non-electrolyte. Before it is possible to interpret the results of conductivity measurements in any given case further investigation is required of the influence of both salts and non-electrolytes upon the conductivity of organic acids, and also of non-electrolytes upon mixtures of these acids and their salts.

For the assumption that the influence of organic acids and salts on the conductivity is small and that the effect of non-electrolytes is usually negligible, Dixon and Atkins claim support from the results of certain experiments of Heald [1902] in which he found that the conductivity of certain plant juices was approximately equal to that of a solution of ash in a volume of water equal to that of the juice from which it was derived.

It must however be remembered that the relation of ash to sap is a very complex matter, and even were there no definite experimental evidence against the conclusion reached by Dixon and Atkins it would be hard to derive support for it from Heald's observations. The ashing of a sap involves a large number of changes which may affect conductivity. These include:

- (1) The destruction of organic acids.
- (2) The conversion of organic salts into carbonates some of which may be insoluble.

(3) The conversion of the metallic constituents of colloid substances (chlorophyll, proteins, pectins) into carbonates or oxides.

(4) The conversion of organic compounds of phosphorus and sulphur into phosphates and sulphates.

(5) The removal of non-electrolytes which reduce the conductivity.

How far these effects balance one another, must be largely fortuitous. In Heald's experiments the conductivity of the ash was usually found to be less than that of the sap, the difference varying from 2 per cent. to over 20 per cent. In the case of cucumber fruit—the only fruit investigated—the conductivity of the ash was only 60 per cent. that of the sap.

Dixon and Atkins' experiments on the effect of liquid air in rendering protoplasm permeable.

The foregoing considerations throw some light on an interesting series of experiments carried out by Dixon and Atkins [1913] on the differences in plant juices obtained by various methods. In these experiments a comparison was made between the juice from plant organs when pressed without previous treatment and the juice of the same organs when treated by exposure to liquid air before pressing. Determinations of freezing point and conductivity were made and on these were based conclusions as to the relative proportion of electrolytes and non-electrolytes present in each pair of samples. Dixon and Atkins found that in every case the freezing point of the juice from the treated organs was lower than that from the untreated, a clear indication that exposure to liquid air had reduced the resistance of the protoplasm to the passage out of the cell contents. They also found in many cases a corresponding but relatively less increase in conductivity which they interpret as showing that protoplasm in its untreated state is more permeable to electrolytes than to non-electrolytes.

In considering experiments of this nature it is desirable to form so far as possible some mental picture of the actual processes which take place. When living tissue is submitted to pressure it may be assumed that an exceedingly dilute solution of electrolytes will pass out at first, after which, as pressure is increased and a number of the cells are killed or burst, the greater part of their contents will escape. In the case of frozen tissues the cells of which are dead from the first, the escape of cell sap from the material will begin as soon as sufficient pressure is exerted. Dixon and Atkins assume that the difference in the value of the ratio $\frac{C}{\Delta}$ is evidence that a considerable quantity of electrolyte passes through the living protoplasm before it is killed by pressure. The interpretation of this ratio is, however, a matter of some difficulty and a further examination of Dixon and Atkins' work is necessary in order to draw definite conclusions from their experiments.

For this purpose a table compiled by Atkins [1916, p. 118] is quoted below which shows the effect of liquid air on the nature of the sap expressed from various plant organs.

		Δ	$C \times 10^5$	$\frac{C \times 10^5}{\Delta}$
(1)	<i>Hedera helix</i> leaves untreated	... 0.767°	403	5.2
	Same sample frozen	... 1.255°	605	4.8
(2)	<i>Ilex aquifolium</i> roots untreated	... 0.531°	563	10.6
	Same sample frozen	... 0.682°	629	9.2
(3)	<i>Ilex aquifolium</i> leaves untreated	... 0.651°	433	6.6
	Same sample frozen	... 1.130°	619	5.4
(4)	<i>Pyrus malus</i> fruit untreated	... 1.507°	171	1.1
	Same fruit frozen	... 1.919°	161	0.8
(5)	<i>Solanum tuberosum</i> tuber untreated	... 0.523°	555	11.0
	Same tuber frozen	... 0.588°	583	9.9
(6)	<i>Vitis vinifera</i> fruit untreated	... 2.567°	132	0.5
	Same sample frozen	... 3.185°	112	0.3
(7)	<i>Chamoerops humilis</i> leaf untreated	... 0.365°	298	8.1
	Same leaf frozen	... 1.529°	752	4.9
(8)	<i>Beta vulgaris</i> root untreated	... 1.473°	570	3.9
	Same root frozen	... 1.761°	555	3.2

It must be pointed out in the first instance that an increase in the total concentration of the constituents of the sap will not be accompanied by a proportional increase of conductivity, since the depression of the conductivity by non-electrolytes will also be proportionately increased. It is therefore necessary to consider in the first place whether Atkins was justified in the main conclusion which he drew from his experiments, viz. that the sap from the untreated tissue contained a higher proportion of electrolytes than that from tissue which had been previously frozen.

In order to obtain evidence upon this point the assumption is made here that the ratio of electrolytes to non-electrolytes in the two saps of each pair of samples from Atkins' table is the same, and that the relative decrease of conductivity in the sap from the frozen tissue is entirely due to the depression produced by the larger quantity of non-electrolyte it contains. On this hypothesis the amount of non-electrolyte can be calculated if a value be assumed for α . From Arrhenius's equation we have

$$\frac{C_2}{C_0} = \frac{100 - \alpha x}{100}$$

and

$$\frac{C_1}{C_0 p} = \frac{100 - \alpha p x}{100}$$

which gives

$$\frac{C_2 p}{C_1} = \frac{100 - \alpha x}{100 - \alpha p x}$$

where C_2 , C_1 = the conductivities of the saps from the frozen and unfrozen organs.

C_0 = the conductivity of an aqueous solution corresponding to the more concentrated sap.

p = the ratio $\frac{\Delta_1}{\Delta_2}$, which by hypothesis is the ratio of electrolytes and non-electrolytes in the two saps.

x = the percentage concentration of non-electrolyte in the more concentrated sap.

Below are tabulated the values of x calculated from this equation from the values of Δ and $C \times 10^5$ observed by Dixon and Atkins and quoted above; the value assumed for α is 2.

Table VI.

	Δ_1	Δ_2	$C_1 \times 10^5$	$C_2 \times 10^5$	x %	x^1 %*
<i>Hedera helix</i>	0.767°	1.255°	403	605	9	12
<i>Ilex aquifolium</i> roots ...	0.531°	0.682°	563	629	20	6
leaves	0.651°	1.130°	433	619	17	10
<i>Pyrus malus</i> '...' ...	1.507°	1.919°	171	161	31	18
<i>Solanum tuberosum</i> ...	0.523°	0.588°	555	583	19	6
<i>Vitis vinifera</i>	2.567°	3.185°	132	112	35	30
<i>Chamoerops humilis</i> ...	0.365°	1.529°	298	752	23	14
<i>Beta vulgaris</i>	1.473°	1.761°	570	555	29	17

* x^1 represents the percentage concentration of hexose the osmotic pressure of which corresponds to Δ_2 . This is added for comparison. The corresponding quantity of cane sugar would of course be nearly double.

It must be remembered that equivalent conductivity will increase with dilution. In the case of acid saps this is very important, for the dissociation of most organic acids increases very rapidly as concentration diminishes. Increased dissociation may thus be largely responsible for the high value of x in such a case as that of *Pyrus malus*, or where the two samples of sap exhibit large differences of concentration.

Bearing these facts in mind a comparison of the values of x and x^1 does not appear to justify Dixon and Atkins' general conclusion that the proportion of electrolyte to non-electrolyte is higher in the saps from the untreated than in those from the treated tissues. In the majority of cases the differences observed in the ratio $\frac{C}{\Delta}$ can with great probability be accounted for by the fact that the electrolytes in the less concentrated saps are more highly dissociated and are subject to the action of a smaller quantity of non-electrolytes. In one or two cases, however, and notably those of *Ilex* and *Solanum*, it appears to be necessary to assume that there is an appreciable difference in the ratio of electrolyte to non-electrolyte in the two saps. This may be due to the expression of electrolyte from the untreated tissue before this becomes permeable to the other constituents of the cell sap as Dixon and Atkins assume, but it is clear that the same effect would be produced by the filtering out of non-electrolyte from the untreated tissue. If substance of high molecular weight were thus removed a considerable increase of conductivity might be produced while the accompanying change of osmotic pressure would be small and a small difference in concentration would accordingly account for the results obtained¹.

¹ It will be noticed that in three of the examples quoted from Atkins' table the conductivity of the sap from the frozen organ is less than that from the same organ untreated. It is suggested by Dixon and Atkins [1913, p. 430] that this is probably due to actual differences in the sap from different samples of the same organ, but that part of the effect may be due to viscosity. Differences of this magnitude would invalidate any conclusions that might be drawn from the experiments. It is however clear from the foregoing that it is entirely unnecessary to assume such differences.

One other point merits some further consideration. There is no doubt that the colloidal constituents of the sap tend to be filtered out in pressing and it is probable that the sap from treated tissues contains more of these substances than that from the untreated. It is therefore natural to suppose that this fact may provide an explanation of those cases in which the ratio of electrolytes to non-electrolytes varies in the two saps.

The case of *Solanum tuberosum* suggests the action of dextrin and it is natural to expect that pectin may exert a similar influence. There is, however, considerable doubt as to the part played by colloids in this respect, and Atkins has pointed out that the viscosity of solutions of this nature is not a measure of their influence upon conductivity. He instances the well-known case of gelatin gels and he describes an experiment in which a pectin solution was gelatinised and its viscosity therefore largely increased, while its conductivity remained unchanged. Atkins draws the conclusion that the effect of pectin upon conductivity is negligible and that this is true for the whole class of substances to which pectin belongs—this, however, is to go beyond the facts. Emulsoid colloids are two phase systems the two phases of which consist of solutions of the colloid in water and of water in the colloid. Conductivity appears to be conditioned by the composition of the more liquid phase only, but as this may contain a considerable quantity of the colloid the effect on conductivity may be far from negligible. All that Atkins' experiment appears to show is that the gelatinisation of pectin is a process which leaves the more liquid phase unchanged. It must be remembered, however, in regard to pectin that it has been observed to possess acid properties. Pectin and its salts may, therefore, have some conducting power in solution which will tend to counterbalance their effect on other electrolytes.

Until the action of colloidal substances has been further elucidated the complete interpretation of such observations as those of Dixon and Atkins cannot be attempted. It may however be stated with some assurance that their results indicate that in most cases the difference in the ratio of electrolyte to non-electrolyte in the saps from treated and untreated tissues must be very small, and that there is no evidence that any considerable quantity of electrolyte can be pressed out from the living cell. These conclusions are borne out by some experiments of André [1906, 1907] to which Atkins [1916, p. 119] has called attention. André determined the proportion of nitrogen and ash in samples of sap squeezed from various organs by successive pressures of 3, 12.5 and 25 kilos per square cm., and arrived at the conclusion that while the concentration of the substances present in the juice varied as the result of different pressures their relative proportions remained unchanged. The method was not susceptible of great accuracy. Small differences of concentration produced by filtration would scarcely be detected by this method especially if the substances filtered out contained neither mineral matter nor nitrogen. The experiments, however, lend some support to the view that any differences in the composition of the saps are mainly due to

the holding back of non-electrolytes by the untreated tissue in the course of filtration.

The foregoing analysis makes it clear that very great caution is needed in the interpretation of observations of the conductivity of plant saps. Decrease of conductivity may be occasioned not only by the addition of non-electrolyte but even in some cases by the addition of electrolyte, while changes of concentration often produce large changes in equivalent conductivity. It is hardly possible therefore to regard electrical conductivity as being in any sense a measure of content of electrolyte. Comparative measurements must nevertheless be of great value in the study of plant saps where methods are available by which the corresponding conductivity in aqueous solution can be ascertained.

It remains therefore to consider the possibility of introducing a correction by means of which conductivity measurements can be reduced to standard conditions.

Some indication of content of non-electrolyte can be obtained from freezing point determinations, but these are of little value for the present purpose, since change of conductivity is proportional to the actual content of non-electrolyte and not to its molecular concentration, so that *e.g.* a hydrolysis of cane sugar might take place which doubled the osmotic pressure, without producing an appreciable alteration of the conductivity. In saps which contain considerable quantities of sugar density determinations are of more value for this purpose, but the following appears to be the simplest method of determining the value of C_0 for a given sap.

By diluting with water to twice the volume the conductivity of the electrolyte in water is approximately halved and αx becomes $\frac{\alpha x}{2}$. If the conductivity of the diluted sap be then measured we have:

$$C_0(100 - \alpha x) = 100 C_1$$

$$\frac{C_0}{2} \left(100 - \frac{\alpha x}{2} \right) = 100 C_2$$

where C_1, C_2 are the measured conductivities.

From these equations the value of C_0 and αx should be obtained with fair accuracy in those cases in which the degree of dissociation varies very slightly with the dilution. When saps contain any considerable quantity of organic acids it is impossible to assume that the conductivity is halved by diluting to twice the volume. In these cases the matter is far more difficult especially as the degree of dissociation of the acid and consequently the effect of non-electrolytes upon it will be largely determined by the amount of salts present in solution.

Further study of the action of both salts and non-electrolytes upon the conductivity of organic acids is necessary before helpful suggestions can be made in this connection.

SUMMARY.

1. Attention is drawn to the effect of non-electrolytes on the conductivity of electrolytes and a paper of Arrhenius is summarised in which the effect is investigated and its magnitude given for various cases.

2. An examination is made of the causes of the low values obtained in conductivity measurements in fruit juices containing considerable quantities of organic acids. It is pointed out that these low results must be ascribed to the action of non-electrolytes and of salts, but that further investigation of the mutual action of these two factors is necessary.

3. An attempt is made to estimate the influence of non-electrolytes and of the changes in the degree of dissociation produced by dilution in certain results obtained by Dixon and Atkins when comparing the saps obtained from frozen and unfrozen plant tissues. It is suggested that there is very little evidence for the marked differences which they assume to exist in the proportional composition of the two kinds of saps. It is further suggested that these experiments afford no evidence that the protoplasm of the cells of tissue under pressure is permeable to electrolyte to any considerable extent.

4. A formula is suggested by means of which in certain cases conductivity measurements may be reduced to standard conditions.

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