table[8], and values of $(-\log_{10} 0.892\, T_S)_{\text{curve}}$ were read from the original large scale plot of Fig. 1.

The results are shown in Fig. 3. To assist in a ready understanding of this figure it may be noted that if the points plot above the horizontal line the oils are lighter than are the Lovibond 3-glass combinations having the same chromaticity; if below the line the oils are darker than the glasses. If the points are to the right of the vertical line the donor graded the oil too red, that is, he assigned a Lovibond red numeral higher than was obtained by the spectrophotometric method; if the points are to the left of this vertical line, he assigned too small a Lovibond red numeral to the oil.

If there were correlation between the two sets of differences the points should be distributed in either pair of diagonal quadrants. If, because an oil is light, the donor assigned it a Lovibond numeral that was too low, and correspondingly if he assigned too high a numeral because the oil was dark, then the points should be grouped in the upper left and lower right quadrants. If the converse were true, the points should be grouped in the other two quadrants. From the graph it is obvious that no such groupings exist, and it may be concluded at once without computing the coefficient of correlation that no significant correlation is to be found.

IV. CONCLUSIONS

It may therefore be concluded that the oil chemists have been justified in stating that the lightness or darkness of an oil is disregarded in giving the oil a Lovibond grade. However, this conclusion must be qualified in two respects: (1) It is based on data obtained about 20 years ago. It is possible, though hardly probable, that changes of personnel, instrument or technique would so affect the readings that a significant correlation might be obtained at the present time. (2) The lack of correlation shown is an average effect. It is not impossible that a single observer or laboratory would show a correlation of the type considered here.

However, the data presented in Fig. 3 would probably justify the oil chemists, in those cases where disputes arise, in accepting values of N″ obtained by the spectrophotometric method with no weight being given to the luminous transmittance of the oil. Many details would of course have to be considered before any such procedure could be put into effect. In particular the method would have to be enlarged to include evaluation of the oils in terms of Lovibond red and other than 35-yellow. Data are on file in the bureau by means of which such evaluation could be made if at any time it is seriously proposed to adopt this method of settling disputes.

REFERENCES

[1] McNicholas, H. J., The Color and Spectral Transmittance of Vegetable Oils, Oil and Soap **12**, 167 (1935); J. Research NBS **15**, 99 (1935); RP815.

[2] This observer and coordinate system are defined in terms of data published in 1922 in the Report of the Colorimetry Committee of the Optical Society of America (J. Opt. Soc. Am. and Rev. Sci. Inst. **6**, 527; 1922). Details of the computational procedure may be found by reference to the more recent bureau publications on Lovibond glasses and vegetable oils. Although a slightly different observer and a greatly different coordinate system are now in common use in colorimetry, known as the 1931 I. C. I. observer and coordinate system, the bureau's work on Lovibond glasses and vegetable oils will continue to be expressed in terms of the O.S.A. data for the sake of continuity with previous work. The values of N″ for either glasses or oils would not be importantly changed if recomputed by way of the I.C.I. data.

[3] See footnote 16 in McNicholas's paper.

[4] See, for example, Rules Governing Transactions between Members of the National Cotton Seed Products Association, Inc.; and Report of the (A. O. C. S.) Uniform Methods and Planning Committee, Oil and Soap **10**, 130 (July, 1933).

[5] See, for example, Geraldine K. Walker, Statistical Investigation of the Uniformity of Grades of 1,000 Lovibond Red Glasses, J. Research NBS **12**, 269 (1934); RP653. The complete list of bureau publications on Lovibond glasses and vegetable oils may be obtained from NBS Letter Circular LC-398, obtainable from the bureau on request.

[6] Kasson S. Gibson and Geraldine Walker Haupt, Standardization of Lovibond Red Glasses in Combination with Lovibond 35-yellow, Oil and Soap **11**, 246 (1934); J. Research NBS **13**, 433 (1934); RP718.

[7] RP653, p. 281.

[8] The sunlight transmittance of oil No. A 17 should be 0.050, instead of 0.504 as given in column 3 of the table; it is correctly plotted, however, in Fig. 8 (top).

NOTES ON THE DETERMINATION OF THE ALKALINITY OF SOAP SOLUTIONS

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ALL who have attempted to study the alkalinity of soap solutions know that there are inherent difficulties in the procedure, and that while it is easy to get a reading to 0.1 pH unit, it is quite another thing to be sure that the reading tells the true story. Independent workers, both honest and capable, are more than likely to get divergent results when dealing with commercial soaps unless they use identical methods and apparatus in making their determinations, and there is wide difference of opinion as to what the best methods and the best apparatus are. Such solutions belong in the alkaline range, the range which is most difficult to study experimentally. They are sensitive to the action of CO_2. They are sometimes colored, usually more or less turbid, and frequently heterogeneous. Various mixtures of alkaline salts or "builders" are frequently present, while the soap itself is a mixture of the salts of various fatty acids, some saturated, some unsaturated, ranging from 10 to 18 or more carbon atoms. The equilibrium between neutral soap colloid, ionic micelle, and true crystalloid is slow of attainment; it is the same for no two of these soaps, and of course differs with change in temperature, dilution, etc. For these and other reasons, no current method of determining the hydroxyl ion concentration of these solutions can be considered truly satisfactory. Even the best of them have certain limitations that should be recognized. Whatever method is chosen, it is important that the difficulties to be met with, the uncertainties involved, the sources of error, and the probable accuracy of the final result be the subjects of careful consideration.

The Colorimetric Method

The colorimetric method is the oldest, the most widespread in use, and on its face apparently the easiest and quickest way in which to determine alkalinity. It does not necessarily follow, however, that it is the best, nor for that matter that in the long run it is the quickest or easiest. Much depends upon circumstances. Where rapidity and no great accuracy are required, it is easy to add a few drops of indicator to a test tube of the solution in question, estimate the color, and jot down a pH value in the notebook, but the reading so recorded *may* be a whole pH unit in error, due to any one of a dozen causes. Such a colorimetric determination *can* be made with a fair degree of accuracy, by proper choice of the indicator, control of volumes and lighting, preparation of suitable standards, and knowledge of the effect of salt content, temperature, etc. That is, a fair degree of accuracy may be had, but only at the expense of the speed and ease and simplicity which originally recommend the method. Probably the greatest danger involved in the use of indicators is the temptatoin *not* to take the time nor exercise the care that are essential, and that one willingly gives to the more complicated apparatus and more imposing technique of other methods. The colorimetric method is by no means simple or easy, but it should not be condemned because of the purely human frailty of refusing it the refined technique and painstaking study accorded to other methods.

The colorimetric method does labor under some severe handicaps, however. In the first place, there is great dearth of indicators for the more alkaline ranges, above pH 10. A satisfactory indicator should undergo a sharp color change over a narrow pH range, yielding colors that are vivid and that do not fade rapidly; it should be stable against decomposition and against precipitation, and it should not be excessively adsorbed by a precipitate or a colloidal phase; it should not exhibit a "salt error"; and in many cases it is essential that it be stable at high temperatures. Such indicators are few in number.[1]

Difficulties like that of matching the color of the soap solution with that of the standard are obvious, but equally serious are certain less obvious frailties of the method. For example, in order to obtain the maximum color intensity (and this is always the goal) a higher concentration of indicator is required in buffers and soap solutions than in NaOH solutions,[2] and since the indicator itself is usually either more acid or less acid than the solution to be tested, rather complicated procedure is necessary to avoid changing the pH of the solution by the addition of the very indicator which is to measure that pH. Especially is this of importance when adsorption by the colloidally dispersed soap, or the dirt in the soap solution, causes progressive weakening of the color and seems to call for larger and larger additions of indicator, or when high temperature causes fading, which one naturally tends to remedy by more of the indicator.

Variations in temperature may be the source of more serious error. A given color at one temperature does not mean the same pH as the same color at another temperature. Thymol blue, for example, has a certain color in a certain concentration in a buffer of pH 9.4 at ordinary temperature. But at 70° C., it will show that same color in a solution of pH 9.0.[3] Stating the temperature problem slightly differently, when thymol blue gives the same color at 90° that it does at 20° C. in the same solution of NaOH,[2] we are likely to be misled into the belief that the alkalinity is the same in the two cases. In reality, the H^+ ion concentration is some hundred-fold greater at the higher temperature, due to the increased dissociation of water itself. As a general rule, heating a solution of NaOH causes a decrease in the characteristic alkaline color of any indicator put therein.

The laundryman is primarily interested in the pH of his washwater as it actually is in the wash wheel, not as it is after the solution has cooled down to room temperature. The soap chemist cannot be content to confine himself to temperatures of 20° or 30° C. Often he must find indicators whose behavior of high temperature is known.

The color standard with which the sample is compared either is, or is based upon, a solution of NaOH or a buffer of known pH. Unfortunately, few indicators show the same color in a buffer solution, and in a solution of pure NaOH of the same pH. Thymol blue, for example, gives the same color at 18° C. in NaOH solution of 10.14 pH, in a glycine buffer of 8.93 pH, and in a borate buffer of 8.60 pH.[2] The color of the indicator is in most cases determined not by the H^+ ion concentration alone but by the concentration of other ions as well. It will vary with the concentration of NaCl, for example. Of course the e.m.f. readings with a hydrogen electrode may vary also, but we attribute this to changes in the activity of the H^+ ion, or in other words, to actual changes in the pH of the solution, for pH values are *by definition* based upon e.m.f. readings. Any failure of the indicator's color changes to parallel the e.m.f. readings is put down as the salt error of the indicator. Few indicators which have been standardized by comparison with the hydrogen electrode in solutions of one salt content will agree with it in solutions of another salt content. And even though, in McBain's studies of a large number of indicators in the alkaline range, only alizarin yellow G, tropeolin O and thymol violet gave the same color in buffer solution and in NaOH solution of the same alkalinity at one temperature,[2] it does not follow that they would do so at another. The error involved is frequently serious, and may easily amount to as much as one or two whole pH units.

McBain's aim, in the work just referred to, was to find satisfactory indicators for soap solutions, but his success was not great. Of all which he examined, phenolphthalein and alizarin yellow G were the best.[4] Most of the others showed errors which might easily amount to 0.5 pH unit, while some (phenol red, for example) were in error by 2 whole pH units, corresponding to a 10,000 per cent error in OH^- ion concentration.[2] Phenolphthalein changes color through a pH range which is rather low for soaps, while alizarin yellow unfortunately does not have a sharp color change, the distinction being yellow vs. orange. With care, results with indicators can be made to agree with electrometric measurements within 0.2 or 0.3 pH units, but it is doubtful if much colorimetric work with soap solutions exceeds this degree of accuracy.

Ultrafiltration and Catalytic Methods

Both the ultrafiltration[5] and the catalytic[6-7] methods are laborious, of a low order of accuracy, and of value chiefly for academic purposes, to serve as an independent check upon other methods. They will not be discussed here.

Electrometric Methods

Electrometric methods have been applied to soaps with more or less success. The quinhydrone electrode is practically excluded from this field because the ionization and decomposition of the quinhydrone itself become so marked at a pH of 8.5 or 9 that at higher alkalinities it is useless. It can therefore be applied only to very dilute solutions of soap.

The Antimony Electrode

The antimony electrode holds greater promise, although neither theory nor practice have been perfected in this case. The potential of this electrode is proportional to the hyrogen ion concentration, or activity, to be more exact, or

$$\text{E.M.F.} = a + b\ (\text{pH}),$$

a and b being constants, and a straight line should result when the e.m.f. is plotted against the logarithm of the H^+ ion concentration. A straight line with the theoretical slope actually has been obtained by Roberts and Fenwick[8] over the range from pH 1 to 10, but many other workers have not succeeded so well. Gysinck,[9] for example, found a kink in the curve, the slope below pH 7.12 corresponding to 58.1 millivolts per pH unit, and above 8.17, 57.6 millivolts. Kolthoff and Hartong[10] had similar difficulty. Between pH 1 and 5, they found a slope of 48.5, compared with 57 demanded by theory, and above pH 9, their slope was 53.6. Between pH 5 and pH 9 results were erratic. The opinion is generally held that the antimony, in contact with air and water, is continuously oxidized, trivalent Sb, pentavalent Sb, and a product showing peroxide properties all being formed, and further, that the nature of the oxidation product affects the e.m.f. It will be noted that Roberts and Fenwick, who obtained good results, worked with the complete exclusion of oxygen, and always approached equilibrium from the alkaline side, and this has been our own practice.

Another trouble with the antimony electrode was brought to light by Holmquist,[11] who obtained one type of curve for HCl and HBr, and another type for H_2SO_4 and $HClO_4$. Our own work has not been sufficiently extensive to justify positive statements, and our results have probably been complicated by the high temperature used. The superiority of this particular electrode over most of the other metal-oxide combinations is probably due to the insolubility of the antimony oxide at low temperatures. But when the temperature is raised to 25° C., and the alkalinity of the solution is higher than about pH 10.5, OH^- ions are used up in dissolving Sb_2O_3 to form antimonite ions.[12] Our experience with unbuffered NaOH solutions at high temperature indicates that the alkalinity decreases with time, but that the change is not so fast as to necessitate rejecting the electrode on that account.

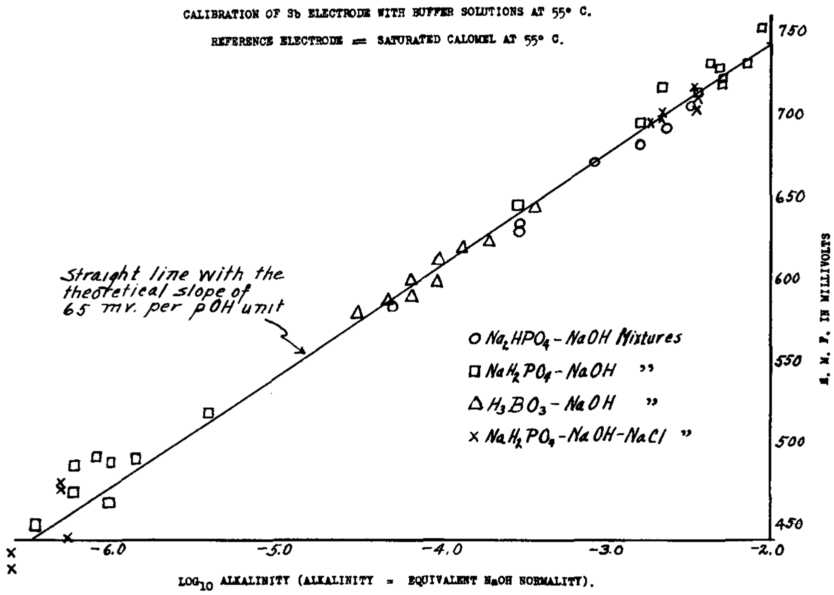

FIGURE 1

A calibration of the antimony electrode at 55° C. in our laboratory by Mr. Oscar T. Quimby, is shown in Figure 1. The equivalent NaOH normalities were determined by means of the hydrogen electrode. The points scatter rather badly, especially those with mixtures of NaH_2PO_4 and NaOH. Here an error of 0.3 pH unit might well occur. Doubtlessly more concordant results could have been obtained had Mr. Quimby been able to work longer on the problem, for most investigators claim an accuracy of 0.1 pH unit or better, *each under his own conditions.* It must be noted, however, that despite these claims to accuracy, the e.m.f.-pH curves of different investigators often differ in position by as much as a whole pH unit.

The antimony electrode is often painfully slow in reaching equilibrium, and the salt error with it is likely to serious. Bodeforss and Holmquist,[13] for example, found that as the KCl content was raised from 0 to 1 normal, the e.m.f. in 0.1 normal HCl fell from 192 to 125 mv., while King[14] over a wide pH range, obtained parallel e.m.f.-pH curves about 0.4 pH unit apart, one in the presence of 1 normal KCl, and one in its absence. When dealing with soap solutions, we are not concerned with normal or even 0.1 normal salt concentrations, but even with soap solutions such as might occur in laundry use, the magnitude of the salt error is not easily predicted. With 0.01 molar $Na_2HPO_4 + 0.005$ molar NaOH, we found that making the sample 0.07 molar (0.4 per cent) in NaCl reduced the e.m.f. by only 1 millivolt, but with 0.01 molar $NaH_2PO_4 + 0.005$ molar NaOH, a reduction of 30 millivolts was caused by the NaCl.

While our own work has not been extensive enough either to condemn or to commend the antimony electrode, it has at least convinced us that there are dangers of serious errors in its use, and until these are eliminated one must go slowly.

The Glass Electrode

Somewhat the same comments apply to the glass electrode, although under certain conditions it has advantages over every other known means of measuring hydrogen ion concentration. It develops its full e.m.f. almost instantly; it does not contaminate or alter the sample; it is unaffected by oxidizing or reducing agents, by colloids or proteins; it can be used with viscous solutions or even pastes; color and turbidity are immaterial. Over a wide range it is affected little or not at all by any ion other than H^+ ion. Nevertheless, it has its limitations, and unfortunately, these limitations apply just where they are most embarrassing to the soap chemist.

When the H^+ ion concentration is different on the two sides of the glass membrane, a difference in potential between the two sides results, but because the resistance of the glass is so high, only a minute amount of current can flow from one side to the other. This makes measurement difficult, and it is common to use either a very thin (and therefore fragile) membrane with a very sensitive galvanometer, or a thicker and sturdier membrane with vacuum tube amplification. Both types are on the market, if one does not wish to build his own.

At 25° C., the H^+ ion concentration is related to the e.m.f of the glass electrode-calomel half-cell system by the standard formula,

$$pH = (E_{obs.} - E_{cal.} + E_1) \div 0.05915$$

where $E_{obs.}$ is the observed e.m.f., $E_{cal.}$ is the e.m.f. of the calomel half-cell, and E_1 is a factor combining the liquid junction potential, the potential of the metallic electrode and solution within the glass electrode, and the so-called asymmetry potential of the glass, to which reference will be made later. Over a limited pH range, this equation holds without error. But as the H^+ ion concentration decreases, as the temperature rises, and as the concentration of certain other ions increases, errors begin to appear. There is a certain constant error for each membrane when made, termed the asymmetry potential, and traceable to the peculiar surface structure of that particular membrane. This error can be corrected by the zero setting, and it seldom amounts to more than a few millivolts. It varies with the age of the membrane, and so the zero setting must be made anew from day to day. More serious is the solvent action of alkaline solutions which gradually change the surface conditions and eventually necessitate discarding the electrode. This action is of course greater the higher the temperature and the higher the alkalinity. With unbuilt soaps the troubles resulting are not marked, but with highly built soaps, at temperatures found in the laundry wash-wheel, it is likely to become a factor of importance. Added to this is the possible reaction of sodium silicate with the glass in the case of highly silicated soaps. To the writer's knowledge, this feature has not been investigated, but a study of the serviceable lifetime of a glass electrode in hot solutions of sodium silicate would be well worth while.

One of the most serious drawbacks to the use of this electrode with soap solutions is its salt error. Neglecting the acid pH range, where the error is less serious, the e.m.f. of the cell at room temperature is a function solely of the H^+ ion only up to a pH of about 8. Thereafter, other ions present in the solution begin to have an effect, the Na^+ ion in particular being active when the usual soft soda glass (Corning 015) is used. Lithium ion is only about half as active as sodium, while potassium ion is still less active. Conversely, if lithium be substituted for sodium in the glass formula, a membrane can be blown which will show far less error due to the Na^+ ions in the sample to be tested. Correction curves for solutions of various pH values and containing increasing amounts of sodium ion have been worked out at room temperature, to show the order of magnitude of the sodium error. Fig. 2 shows such a set as furnished by the makers of the Beckman instrument, the curves being based upon Dole's work.[15] The recommended practice is not to use approximate correction curves, however, but to standardize the glass electrode with a buffer solution of the same pH and the same Na^+ ion content as the sample to be studied. This sounds simple, *provided* one knows the Na^+ ion concentration in the sample—which very frequently one does not know. The field of usefulness of an instrument is greatly restricted if it cannot be used with a sample of unknown composition.

This set of curves (Fig 2) shows two trends of importance. First, the error becomes greater the higher the salt concentration, and second, it becomes greater the higher the alkalinity. Thus a 0.25 per cent solution of coconut oil soap, having a pH of 9.5 or 10, would be only about 0.01 normal in Na^+ ions, assuming complete ionization of the soap. At 25° C. at pH 10, this concentration of Na^+ ion causes negligible error. If we are dealing with a liquid soap base containing 25 per cent coconut oil soap, the concentration of the soap, and therefore of sodium, is approximately 1 normal, but the soap is predominantly in colloidal form, so that the sodium *ion* concentration is still small, and again the salt error at 25° C. is not serious. If the soap is highly built, consisting, let us say, of two parts of soap to one part of soda ash, and if it is being used for washing in hard water, a total concentration of 0.5 per cent is not excessive. The carbonate alone in such a solution would bring the pH to well above 10, but the Na^+ ion concentration from both carbonate and soap combined would not exceed 0.05 normal. Thus, once again, the salt error would not be very great.

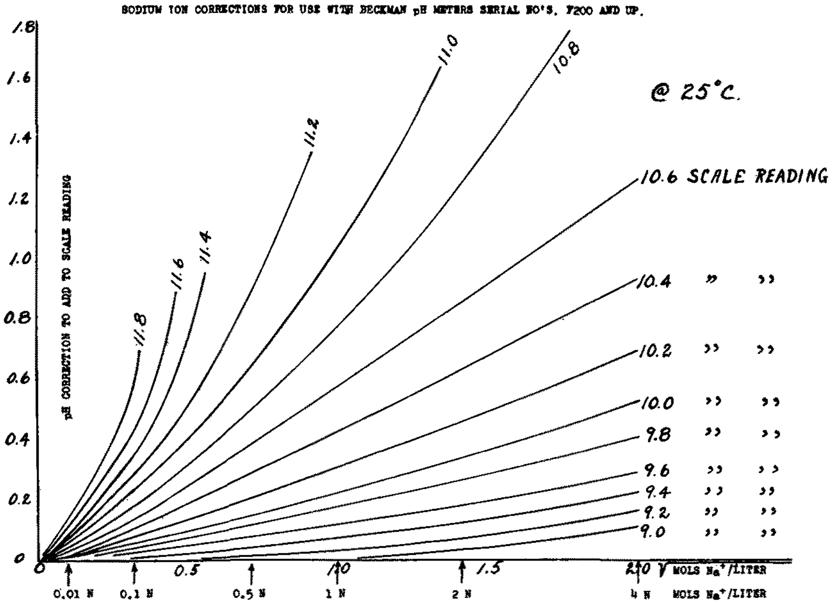

FIGURE 2

On raising the temperature, however, the picture changes, for the salt error then becomes more marked, both in magnitude at a fixed pH, and in manifesting itself at a lower pH. With the Leeds and Northrup electrode, Gardiner and Sanders[16] have shown that at an observed pH reading of 8.5, the addition of 2 normal Na^+ ion necessitates a correction of less than 0.25 pH unit at 30° C.; of 0.5 pH unit at 50°, and of 1.5 pH units at 60°. Furthermore, at 60° the error begins to appear at as low as pH 5, and it becomes so great as to make worthless any measurements above a true pH of 10. Even at 50°, the potential of the glass electrode at pH 11 is almost independent of pH, and changes linearly with the p Na of the solution. It thus ceases to function as a hydrogen electrode at elevated temperatures when the concentration of H^+ ions is low and that of other ions high. Recent work at 50° C. by Dole[17] indicates that at a true pH of 11, the addition of 0.1 normal sodium ion reduces the apparent pH by nearly 0.5 units, while at a true pH of 12 the error is practically doubled. With soaps of low alkalinity, at low temperature, and at low concentrations of Na^+ ions, the glass electrode is a useful and convenient instrument, but under other conditions its reliability has not yet been established.

The Hydrogen Electrode

There remains the hydrogen electrode, the standard of pH measurements, on which all pH readings ultimately rest. It, too, has its limitations, but these are on the whole probably less numerous and less serious than those inherent in the other methods of measurement which have been described, in their present state of development. For example, the hydrogen electrode is assumed to be independent of the presence of salts in the solution. True, if NaCl is added to a buffer, the apparent pH may decrease. But what is considered "salt error" in other methods is not considered "salt error" with the hydrogen electrode. This is by definition, for pH is best defined not as the logarithm of the reciprocal of the H^+ ion concentration, but as a mathematical quantity based upon e.m.f. readings with the hydrogen electrode. These readings are thought to be a measure of H^+ ion activity. If they are lowered by the addition of NaCl, we say that the pH is actually lowered, and we interpret this as meaning that the H^+ ion activity has been lowered thereby. Any other method of measurement which does not give the same pH values as the hydrogen electrode, upon the addition of salt, is said to have a "salt error." Obviously, then, the hydrogen electrode has the advantage over the others in this respect.

There are, however, certain other weaknesses of the hydrogen electrode which becomes apparent with soap solutions. One of these is the slowness with which the equilibrium is reached. A hydrogen flow of from 10 minutes to an hour or more may be required in order to get a steady reading. Aside from the natural dislike of so tedious a measurement, this slowness gives rise to other troubles. When hydrogen is bubbled through soap solutions, they foam, and the ratio of fatty acid to Na_2O in the foam is higher than in the solution in bulk. Thus if fatty acid is continuously being removed in the foam during an hour's hydrogen flow while waiting for the equilibrium to be reached, the e.m.f. will vary continuously as the composition of the liquid bathing the electrode varies. The most obvious way in which to avoid this difficulty is to use a closed, rocking type of electrode vessel, from which no foam escapes. Whether or not this refinement is required depends upon the degree of accuracy desired.

Another possible source of error is not so easily escaped. When unsaturated soaps—and practically all commercial soaps are to some degree unsaturated—are in contact with hydrogen gas and platinum black, hydrogenation at the double bonds occurs to a greater or less extent. This means that the alkalinity measured is higher than the true one, since saturated soaps are more highly hydrolyzed, and therefore more alkaline, than unsaturated ones. Thus at 90° C., the OH^- ion concentration in 0.01 normal sodium stearate is 0.0013 normal, while with sodium oleate it is only 0.0008 normal.[4]

TABLE 1

E. M. F. readings with a 0.05% solution of soap, using the hydrogen electrode vs. the saturated calomel half-cell, both at 55° C.

H_2 Flow (Minutes)	5	10	15	20	25	30	35	40	50	60
E. M. F. (Millivolts)	684	769	721	738	745	750	755	758	762	766

The rise in e.m.f. resulting from the hydrogenation may be to some extent balanced by an opposing tendency, namely, reduction in effective hydrogen concentration at the electrode surface. Nevertheless Bleyburg and Lettner[18] found pH values of 7.3 to 7.8 for soaps from unsaturated oils by the hydrogen electrode at 90° C., and 8.65 to 8.85 for the same solutions by the indicator method. This might be attributed to indicator error, but with palmitates and stearates the colorimetric and the electrometric values agreed within 0.2 pH unit for the same solutions. The hydrogenation is more rapid at high temperature, but it also seems to occur at low temperature, and here another complication arises, for the investigators just mentioned found that at low temperature the saturated soaps formed by hydrogenation tended to coat the surface of the electrode with an insoluble film, which prevented its further functioning.

Our own experience with the hydrogen electrode tends to minimize the seriousness of the hydrogenation and foam errors, and of the slowness with which equilibrium may be reached. As to the last, the time required cannot be definitely stated. It varies with the temperature, the rate of flow of gas, the type of vessel, the age and activity of the electrode, the alkalinity of the solution, and the concentration of soap, the higher these latter two the shorter the time required. At 55° C. with the alkaline builders, with built soaps in general, and with high concentrations (above 0.2 per cent) of unbuilt soap, readings are as high after 10 minutes as after a longer flow of hydrogen, and these readings are in general reproducible. On the other hand, with sluggish electrodes, and with only a few hundredths of a per cent of unbuilt soap, readings are not easily reproducible, and vary with the duration of hydrogen flow, as illustrated by Table I.

Hydrogenation of double bonds could not bring about such large e.m.f. changes as these, nor could we, for other reasons, accept without question a hydrogenation explanation, since very similar results were obtained with sodium laurate, the hydrogenation of which is impossible. The rise in e.m.f. might be attributed to gradual removal of acid soap in the foam were it not for the fact that, at 0.05 per cent concentration, no foam was formed. In fact, it is reassuring as to the hydrogen electrode that the low concentrations of unbuilt soaps, with which it is most difficult to get reproducible results and which show the greatest time lag, are not of great practical importance, since such solutions are not capable of washing or sudsing. On the other hand, when the concentration is raised to the useful washing and sudsing range, equilibrium is attained rapidly, and results are reproducible.

When e.m.f. is plotted against concentration of soap, the curve rises rapidly at first, but at 55° C. it soon flattens out, so that further additions of soap have little effect in increasing the alkalinity. Of course at very high concentrations, measured in whole per cent rather than tenths of a per cent, the alkalinity eventually falls again, due to greatly decreased hydrolysis of the soap.

The behavior of the built soaps is interesting, especially in hard water. When the builder is NaOH, the alkalinity is practically that of the NaOH alone, unaffected by either the soap or the hardness. When Na_3PO_4 or Na_2CO_3 are used, the alkalinity at high concentrations is again that of the builder alone, but at low concentrations the alkalinity is (a) greater than that of the builder alone in hard water, and (b) less than that of the builder alone in distilled water. The indication here is that part of the water softening is done by the soap, and part by the builder, the effective concentration of the builder being thereby decreased. In fact, the reduction in alkalinity when the alkaline builders are added to hard water is a hitherto unused tool for measuring the water-softening power of the builder. By comparing e.m.f. readings in hard water with those in distilled water, calculation of the amount of builder combined with the hard water should be possible.

Mixtures of sodium silicate and soap offer some anomalies which are difficult to explain, perhaps because of the difficulty in getting reproducible readings in such systems. Sodium silicate (SiO_2: Na_2O ratio of 3.17) differs from the other alkalis in that it seems to act as a buffer for soap. In some cases it actually reduces the alkalinity of the soap even though the silicate alone is more alkaline than the soap alone.

The Interpretation of pH at High Temperatures

In speaking of soap solutions we have been glibly using the terms "pH" and "alkalinity" without much distinction. There are dangers involved in such a practice. Prof. McBain once wrote: "Here the modern jargon, which speaks of pH instead of alkalinity, is not helpful."[2] It is worth while to ponder on this.

The concept of pH as the negative logarithm of the H^+ ion concentration is easy to grasp, but it is inexact, for we do not know how to measure the concentration of H^+ ions. The actual numerical values called pH are determined by dividing the potential of a hydrogen cell by $\frac{2.3026\ RT}{F}$. It is activity, not concentration, with which we deal, but at least as long as the magnitude of the liquid junction potential of the cell remains in question, the definition of pH is best given in terms of the potential developed by certain electrode systems, the hydrogen electrode and the calomel half-cell being taken as standards. So defined, pH is given by the equation:

$$pH = \frac{E - E_c}{0.00019837\ T}$$

where E is the observed e.m.f. of the system, E_c is the potential of the 0.1 N calomel half-cell relative to the normal hydrogen electrode, and T is the absolute temperature. As the temperature rises, the value of E_c falls, and thus one term of the numerator of the fraction decreases while the denominator increases. Hence if E remained constant, pH would always decrease with rise in temperature. Actually, E does not remain constant, due to changes in the ionization of water and of the electrolytes dissolved therein, or in the activity of the ions. Neglecting the effect of dissolved salts, the ionization constant of water, K_w, increases with rise in temperature, which merely means an increase in both factors of the equation

$$[H^+]\quad[OH^-] = K_w$$

With pure water at 25° C., $K_w = 1 \times 10^{-14}$, approximately, hence the concentration of H^+ ions, and of OH^- ions, is 1×10^{-7}, and so the pH of pure water is approximately 7, the neutral point. But at 55° C., the value of K_w becomes 7.297×10^{-14}, (19), so that at this temperature, the H^+ and OH^- ion concentrations, while still equal, are each equal to $\sqrt{7.297 \times 10^{-14}}$, or the pH falls to about 6.57. Thus the pH of water may decrease, or it may increase, without changing its neutrality, for neutrality is determined not by the concentration of H^+ or OH^- ions, but by the equality of these concentrations. We may speak of a pH of 6.6, and still not know whether the solution is more acid or more alkaline than pure water. We can say that raising the temperature of a soap solution lowers the pH, but do we mean by that that the solution is less alkaline at the higher temperature? Actually, the degree of hydrolysis of soap solutions, and hence the OH^- ion concentration, increases as the temperature rises.

One difficulty lies in our definition of the word "alkalinity." "Definitions," says Hunter, "are the most accursed of all things on the face of the earth." Yet they may be of great help in bringing about clear thinking. By "alkalinity" do we mean the concentration of OH^- ions, or do we mean the excess of OH^- ions over H^+ ions, i.e., the deviation on the alkaline side of neutrality? If we mean the latter, then two solutions of the same normality of OH^- ions will be of equal alkalinity only if they are at the same temperature. If they are at different temperatures, then the one at the lower temperature will be more alkaline, since it will have a larger excess of OH^- ions. Conversely, two solutions of the same alkalinity will have the same normality of OH^- ions only if they are at the same temperature. If they are of equal alkalinity, but at different temperatures, then the one at the lower temperature will have a lower OH^- ion concentration. A completely ionized solution which is normal in H^+ ion or OH^- ion at one temperature will not be normal at any other temperature, even though ionization remain complete.

Again considering only concentrations, and not activities, and excluding the effect of the dissolved electrolyte upon the ionization constant of water, a normal solution of a base, if completely ionized, would have a pH of 14 at 25° C., and of only 13.1369 at 55° C. But it may be a weak base, incompletely ionized at both temperatures, and approaching complete ionization more nearly at the higher temperature than at the lower. In this case its pH will be lower than 14 at 25°, and lower than 13.1369 at 55°, but the deviation from 14 at 25° will be greater than the deviation from 13.1369 at 55°. Thus as the temperature rises, two factors oppose one another, (a) increasing ionization of water, making for lower pH, and (b) increasing ionization of base, making for higher pH.

In addition to the fact that the dissociation constant of water is about 500 times greater at 100° than at 0° C., the presence of neutral salts in solution has an effect.

Thus K_w for 0.5 N — NaCl solution is about twice that for pure water,[20] which means that the OH^- ion concentration is about 1.5 times as great. But since the H^+ ion concentration is also 1.5 times as great, the pH is actually lower in the salt solution, even though it is still "neutral."

It is obvious how difficult the interpretation of "pH" becomes at temperatures above room temperature, or in solutions containing salts. For this reason, it is far simpler and much more easily comprehensible for practical purposes, to express the alkalinity of a soap solution in terms of the concentration of NaOH which at the same temperature will produce the same e.m.f. reading with the hydrogen electrode. The standard used is then available to all and is understood by all, and if such a standard were in universal use, the literature would not be cluttered up with so-called "pH" readings, the validity and meaning of which will never be known by any but the author.

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THE PIGMENTS OF RYE GERM OIL[*]

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IT IS the purpose of this communication to present the results of preliminary work, based upon the experience of others, on attempts at the development of a procedure for the determination of the carotenoid or polyene pigments of rye germ oil, one which, it is hoped, may find ready adaption to the examination of the germs of other members of the Gramineae as well as to fatty oils in general.

Investigations in this field divide themselves roughly into two classes. One collectively determines all the pigments under one general head as "gasoline color value" or at best utilizes but one of the several components as a measure of the pigments present. The other, an extremely exhaustive one, is time-consuming and, therefore, hardly applicable in the average laboratory. The first group has been developed by Schertz,[1, 2] Bailey and associates,[3-5] Guilbert,[6] and Miller.[7-9] Their methods, however, are restricted by several factors which make them inapplicable for the objective in question. As already indicated, often only the total pigment concentration is determined, or at most but two components thereof, such as xanthophyll and *beta*-carotene. Furthermore, since these methods were primarily developed for the examination of pigmented material of low fat content, we have found them to be unsatisfactory when applied to the problem in hand. The second group includes the contributions of Willstätter and Escher,[10] Palmer,[11, 12] and Kuhn and others,[13, 14] investigators to whom collectively belongs the credit for the greater portion of the information now available on the properties, structure, and methods of isolation of the polyene pigments. Since these methods require large amounts of raw materials, with the consequent handling of large volumes of solutions in laboratory glassware of unusual sizes, they hardly lend themselves to analytical procedures although they do have the advantage of successful application to the qualitative determination of all of the known carotenoids.

The polyene pigments, as the name suggests, owe their coloration to an extended system of conjugated double bonds. Just as is the case with many such conjugated systems, these pigments are very susceptible to the action of chemical reagents. Their susceptibility to oxidation makes necessary the elimination of atmospheric oxygen in all quantitative procedures, proscribes the use of any solvent, such as diethyl ether, which has not been freed of peroxides immediately before use, and demands that all analytical procedures require as little time as possible. The polyene pigments readily add other "double bond" reagents and are particularly susceptible to acidic compounds. Thus, if the chromatographic adsorption method of Tswett[15] is employed, it is best to avoid the use of acid adsorbants. Heat and light are quite effective in isomerizing and decomposing the carotenoid pigments, especially in the presence of air and moisture. Therefore, temperatures higher than 45° C. are rarely used when handling these compounds. The polyenes are soluble in the organic solvents; hence, for effecting solution diethyl ether, petroleum ether, chloroform, and carbon disulfide have been most frequently used. Solutions of the pigments in these solvents, with the exception of diethyl ether, are generally conceded to be stable[1, 2] when stored under refrigeration away from light in an inert atmosphere. Carbon disulfide is one of the most efficient of the solvents for the pure pigments, and it was this fact, used in conjunction with the knowledge that carbon disulfide yields an oil high in color value and with a relatively large amount of unsaponifiable matter,[16] which led to the adaption of Miller's method of isolation as a basis

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