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*p*H VALUE AND ITS IMPLICATIONS

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Dr. Marriott gives an easily understood explanation of "*p*H," discussing strong and weak acids and buffer action. The effects of varying the *p*H value on protein structures are used as examples of its importance to cosmeticians. A simple method of assessing the extent of buffering action is given and the behaviour of indicators and their selection for particular purposes is described. The precise understanding of the meaning of the *p*H value is stressed throughout.

THE SUBJECT of this address was chosen as it appeared to me that the occasion of the President's address was a suitable one on which to talk on a matter which was tending more and more to become misused. It is quite clear that the notation of *p*H value is slowly losing its precise significance and is becoming contracted to the simple term "*p*H," which is often quite meaningless and unreal. There is no such thing as "*p*H," but there is a significant figure known as the *p*H value which is of prime importance to all engaged in industrial chemistry. The *p*H value is a mode of expressing the hydrogen ion concentration of aqueous liquids. The hydrogen ion concentrations, which are obtained when acids or alkalies are added to water, range over concentrations from one to one hundred million millions, and are expressed in negative powers of the base 10, i.e., they are reciprocals, and are not easy to manipulate. The scheme put forward by Sörensen, known as the *p*H scale, simplifies the matter. The *p*H scale is, however, simply a mode of expression.

It is necessary for me to give a very simple and brief outline of the basic theory underlying this conception. Historically, the notion that all chemical reactions depended on the dissociation of substances into charged atoms dates back to the middle of the nineteenth century, but the hypothesis proved to be full of complications. It can be said, however, that clarification, at any rate in respect of reactions in solutions, dates back to Arrhenius who, in 1887, laid the foundations of the concept of hydrogen ion concentration. This breakdown or dissociation of molecules is electrolytic in character, the charged units being called "ions" which can be either single atoms or small groups of atoms (radicals) or larger co-ordinated groups (complexes). The term "ionisation" should, perhaps, be employed to describe this process in contrast with dissociation, which is the simple breaking down of a compound into two or more components which may or may not be electrically charged.

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In the early days, and even in relatively recent times, many objections were made against this idea, notably by the H. E. Armstrong school, but as time went on and knowledge increased the reality of ionisation became more and more established. The discovery of the electron by J. J. Thomson in 1897 laid the foundations of modern atomic structure and gave reality to the charged particle. Following the isolation of radium by the Curies and the outstanding work of Moseley, Rutherford and, later, Bohr, were enabled to indicate the principle on which the atom is built. As everyone now knows, the atom consists of a positively charged nucleus surrounded by a dynamic field of electrons. The structure of the field of electrons is known with considerably certainty and the build-up enables the chemistry of the elements to be forecast and, in particular, what happens when the atoms ionise. The loss or gain of an electron produces a positive or a negative charge and the modern conception of chemistry, especially in the organic field, is based on this phenomenon.

To understand the basic theory of hydrogen ion concentration, it is necessary to consider the physical chemistry of water. It is known that pure water, although a poor conductor, nevertheless conducts electricity and that the passage of an electric current produces hydrogen at the cathode and oxygen at the anode. The breakdown of water into hydrogen and oxygen is facilitated by adding an electrolyte of suitable character so that the conductivity, or the number of ions per c.c., is significantly increased. From the law of mass action of Guldberg & Waage, it can be deduced that the ionisation of water, $H_2O \rightleftharpoons H^+ + OH^-$ can be expressed by the simple equation

$$\frac{[H^+] \times [OH^-]}{[H_2O]} = k, \text{ (a constant)},$$

the brackets meaning concentration in moles. per litre. It is known that the ionisation of water is so small that the concentration of un-ionised water is virtually constant and the equation can now be written $[H^+] \times [OH^-] = k_1 \times k_2$. $k_1 \times k_2$ is also a constant and can be written K_w. Thus, we have the equation that $K_w = [H^+] \times [OH^-]$. K_w is the ionisation constant of water. From conductivity measurements, it is known that at 22° C. the K_w of pure water is 10^{-14}; the value varying, of course, with the temperature. For the purpose of this talk, the figure $K_w \times 10^{-14}$ will be used. Bearing in mind that for every hydrogen ion there must be a hydroxyl ion, $[H^+] = [OH^-]$, and, therefore, the concentration of hydrogen ions in pure water is $N \times 10^{-7}$, as is also the concentration of hydroxyl ions.

When an acid is dissolved in the water the hydrogen ions produced by the acid increase the concentration of the hydrogen ions, and because K_w must be constant there is a corresponding decrease in the concentration of OH ions to compensate for the increased acidity. Apart from the mere concentration of the added acid, the change in the ratio of hydrogen to

hydroxyl ions depends on the ionisation constant of the added acid, so that the concentration of hydrogen ions in a tenth normal solution of a strong acid, hydrochloric acid, will be different from that in a tenth normal solution of a weak acid, acetic acid. In the case of hydrochloric acid at $0{\cdot}1N$, the concentration of hydrogen ions will be approximately $N \times 10^{-1}$, whereas in the case of acetic acid the hydrogen ion concentration will be approximately $2N \times 10^{-5}$. This is because weak acids, such as acetic, do not ionise to the same extent as strong acids, and in this lies the difference. As everybody knows, the two acid solutions, if neutralised by means of added alkali, require precisely equal amounts since titration measures the total reservoir of acid, whereas the hydrogen ion concentration measures what might be called the "effective acidity."

The concentration of hydrogen ions can be expressed as a pressure, for it is easy to see that if in one solution of acid in water the concentration of the hydrogen ions is $10^{-1}N$ and in another it is $10^{-5}N$, the number of collisions in unit time with, say, the walls of the container in the one will be ten thousand times that of the other. This view corresponds with the kinetic theory of gases.

This application of the kinetic theory clearly indicates that hydrogen ion concentration is covered by the gas laws. Indeed, the first and, incidentally, the standard method of determining the hydrogen ion concentration was to take a strip of noble metal, e.g., platinum, coat it with platinum black and saturate this surface with hydrogen. When this coated metal is placed in a liquid, it behaves as though the electrode is hydrogen and it will give a pressure of hydrogen ions. Depending on how far the pressure of hydrogen ions in the water can combat the hydrogen pressure due to the hydrogen sorbed in the platinum black, so an E.M.F. is obtained. From this one can, by using the electrical equivalents, calculate the hydrogen ion pressure using the simple gas law formula $PV = RT$ as the basis. It must be emphasised that the gas laws are based on Boyle's and Charles' laws, and are only accurate when applied to low pressures, i.e., equivalent to dilute solutions.

The values obtained, however, relate to molar solutions and are so small that they have to be expressed in terms of negative powers of the base 10. They prove very clumsy when large numbers of solutions are being dealt with or if the values are to be plotted. Sörensen's scheme, put forward in 1909, was to consider all the values in terms of reciprocals of the logarithms to the base 10. That is to say, the logarithm with the sign changed. This notation enables one to see quickly differences in effective acidity, bearing in mind that as one proceeds from one unit of *p*H to another the effective concentration of hydrogen ions has changed ten-fold. Each whole step is ten-fold and mere plotting of *p*H values in uniform intervals does not in any way alter the ten-fold steps. It is merely a convenience.

The *p*H scale led, of course, to a range of values from 0 to 14. (In actual fact the *p*H range is not exactly 0 to 14 : it would be nearer the truth to suggest that it was from − 3 to + 14·5.) This range, however, should not be looked on as being a precise reality when the *p*H values are less than 1 or more than 13, for it must be remembered that the gas laws only hold for ideal gases and when the pressure of a gas is increased (i.e., the concentration), the equation ceases to be accurate for reasons which need not, perhaps, be gone into here. Nevertheless, the point is that the *p*H notation and, indeed, the theory of hydrogen ion concentration can hold only in dilute solution, the limit of accuracy being probably when the concentrations are not greater than N/100, unless the "activity" be used as a correction factor. The need for such a factor indicates the need for caution when very low or very high *p*H values are being handled.

The hydrogen ion concentration concept via the *p*H scale has, of course, been extensively applied to industry. It is interesting to note, however, that the first use was described by Wood, Sands and Law in 1911. They used a very primitive platinum electrode set-up on tanning liquors. As a result of this, the leather industry can be claimed to be the initiators of its industrial application. Its application to protein research was quickly appreciated, and since 1918 many papers have been published on the swelling and the acid and base combinations of fibrous and non-fibrous proteins.

If the *p*H value measures the hydrogen ion pressure or alternatively the hydroxyl pressure, it is quite clearly implied that the reaction between acids, alkalies and proteins must be a direct function of the *p*H value. In the case of hair, the swelling of the protein is never very great, except when the *p*H value is of the order of 10 or more, but even in the case of hair the hydrogen ion concentration does play a part in the water uptake. The proteins collagen, muscle, and, of course, the degradation product from collagen, gelatin, are very susceptible to changes in hydrogen ion concentration. When gelatin is immersed in water containing hydrochloric acid at a *p*H value of 2·4, the swelling can be two or three thousand per cent on the dry weight. With the fibrous proteins the swelling is not so great, although it varies with the age of the animal from which the fibre has been taken. The significance of the small degree of swelling of hair and epidermis in acid and mild alkaline solutions is strongly indicative of the usefulness of this particular protein as a protective surface for the living body.

The living proteins are sensitive to variation in *p*H value and this fact is almost the key to the metabolic processes which take place. Biologically active proteins not only bind large amounts of water, but their sensitivity to swelling with changes in *p*H value is also great.

The swelling of fibrous protein is a very good measure of the biological age of the animal. I use the word "biological" to differentiate between the

simple "years old" by which people are normally defined. It will be well appreciated that amongst men and women and all animals there is a marked difference in their youthfulness, which is a measure of their biological age. In fact, it could quite easily be said that the biological age of a person can be measured by the extent to which the tissues bind water, and this reflects itself by the extent of the swelling of the tissues when in equilibrium with aqueous solutions of different *p*H values.

It must not be believed that *p*H value is the only arbiter of the amount of swelling of a protein. A great deal depends on the anion of the acid or the cation of the alkali which is used in order to create the particular *p*H value. For example, collagen fibres of skin immersed in a solution of hydrochloric acid of *p*H 2·4 will swell significantly more than similar fibres placed in a solution of sulphuric acid at *p*H 2·4. This is due to the valency of the anion which was shown clearly more than 35 years ago by Loeb. In a similar way in the alkaline ranges of *p*H value, a solution of a divalent base, as, for example, barium hydroxide, will only produce about half the swelling of a collagen fibre produced by a mono-valent base of the same *p*H value. Neither will ammonia solutions produce the same sort of swelling at equivalent *p*H values to those produced by potassium or sodium. But then ammonium hydroxide has characters peculiar to itself. It is because of these peculiarities that ammonium compounds, as, for example, thioglycollates, are used in cold waving solutions.

It must not, however, be overlooked that the presence of salts can bring about remarkable changes in the ability of the hydrogen ion concentration to deform protein fibres. This effect is not due to any buffering action. By way of example, it might be mentioned that if a collagen fibre be swollen by dilute hydrochloric acid, the imbibition of water can be completely repressed by the addition of sodium chloride. In the presence of a strong acid and 2 molar sodium chloride the protein will be dehydrated. Such a process has for many decades been employed for preserving unhaired skins, notably sheep skins, the dehaired pelt being soaked in a 1 per cent solution of sulphuric acid in the presence of about 10 per cent of sodium chloride. The pelts in this stage are dehydrated and, provided no water is allowed to come in contact with them to dilute the concentration of sodium chloride, they can be preserved for long periods of time without any ill-effect.

In a similar sort of way, the concentration of salts has to be very carefully controlled in the tanning of leather, as a lack of salts may produce a harsh and unsatisfactory leather, whereas too high concentration of salts will produce too soft a leather. The word "salt" here does not mean only sodium chloride, but salts of other acids and bases, some of which may be organic. The effect of these salts cannot be determined by the *p*H value alone.

In this connection it is also interesting to note that if collagen fibres be treated with solutions of increasing acidity, there is little or no change in

the swelling until the *p*H value is of the order of 4·0. In the particular case of hydrochloric acid it is at this *p*H value that one can distinguish a faint acid flavour. At *p*H values of 4·2 and above, the solutions have no acid tang. A solution more acid than *p*H 4·0, but containing a small quantity of sodium chloride, fails to produce an acid taste. It is the *p*H value coupled with the presence of the various salts in fruit juices which bring about the variations in sourness which have been noted in different fruits by a number of observers. The concentration of ions derived from the acids and bases shows itself in the swelling of proteins quite apart from the buffering effect of these ions in suppressing the ionisation of the acids or bases. The effects of salts, whether or not they have a common ion with the acid or alkali, are quite pronounced and it shows how careful one must be when buffer solutions are employed.

Buffer solutions are very useful when the *p*H value has to be stabilised. For example, if, to a 0·1*N* solution of acetic acid, sodium acetate be added so that the concentration of the sodium salt is 0·05*N*, the *p*H value will increase from 2·8 to 4·4. This is because the added acetate ions have reduced the hydrogen ion concentration in order to make the product of the concentration of these two ions constant. A similar result would be produced if the acid had been, say, half neutralised with caustic soda. At this point small additions of acid or alkali may be made without sensibly altering the *p*H value. Of perhaps still further importance, however, is that such a mixture can be diluted with water without a significant change in *p*H value. This is because the ratio of non-ionised acid to acid ions is the dominant feature and not the absolute qualities. This fact leads to an important differentiation.

A solution of strong acid or base on ten-fold dilution will alter in *p*H value by 0·9 to 1·0 unit.

A weak acid or base on ten-fold dilution will alter in *p*H value by approximately 0·5 unit.

A buffer solution on ten-fold dilution will alter in *p*H value by less than 0·2 unit.

It is often desirable to appreciate quickly the arithmetical equivalent of differences in *p*H value. For example, consider the difference between *p*H 5·0 and *p*H 5·3. The difference 0·3 is the logarithm of 2, so that the higher *p*H value indicates a solution of half the hydrogen ion concentration of the other. Similarly, a difference of 0·5 in the *p*H value is approximately equivalent to a three-fold change in hydrogen ion concentration. A change of 0·6 is indicative of a four-fold increase or decrease in the hydrogen ion concentration, while a difference of 0·7 signifies a five-fold change. An alteration in *p*H value of 0·9 is, of course, three times as great as 0·3, which means an increase in concentration of $2 \times 2 \times 2$ times, or eight-fold.

With these features in mind one is able to make many valuable implications with regard to *p*H values. Whereas a simple *p*H value tells only of the

pressure (concentration) of hydrogen ions or of hydroxyl ions, much more information is needed to give the full and true picture of the system under examination. If the solution be diluted ten-fold the presence of a strong or weak acid is determined. Such an experiment will also indicate whether a good buffer system is in operation, but the system may still be intrinsically of buffer type but produce a change of *p*H simulating a weak acid if additional traces of acid or alkali are added. This is because the titration curve of a weak acid is sigmoid in character and extends roughly over four units on the *p*H scale. The symmetry is centred round the half neutralised point, the *p*H value of which is an accurate measure of the ionisation constant (K) expressed on the *p*H scale, i.e. *p*K. Thus, a weak acid of *p*K 4·7 will be half neutralised by caustic soda at this p*H* value and in tenth normal solution the pure acid will give a *p*H value about 2·7 (actually, in the instance of acetic acid the *p*H value is 2·85). In the range of about *p*H 3 to 4 and 6 to 7 the stability of the buffer system in relation to added acid or alkali will be lessened, but its stability to dilution will be sensibly the same as at the middle range 4 to 6.

The best check on the buffering ability of a solution is to see what *p*H changes occur when a strong acid or alkali is added. Normally this involves a titration curve, but within a given range of *p*H value a quick procedure is to determine the volume of Normal hydrochloric acid (or sodium hydroxide) needed to alter the *p*H value of 100 ml. of the experimental solution by one unit. This quantity can be called the "buffer" index. Bearing in mind the sigmoid shape of buffer solutions, it is advisable to carry out the titration over a range of 2 units of *p*H. Certain solutions do not show much change in *p*H value when small quantities of acid or alkali are added. For example, N/100 hydrochloric has a *p*H value of 2·0, and if 1 ml. of N/10 acid were added to 25 ml. the fall in *p*H value would be 0·15. The same amount of N/10 hydrochloric acid added to distilled water would reduce the *p*H value from 7 to 2, a change of 5 units. This is because the *p*H scale is logarithmic and the change in hydrogen ion concentration is purely arithmetic and its value on a logarithmic base depends on which part of the *p*H scale is in use.

A consideration of the ionisation constants of acids and bases is important in the ordinary laboratory titrations. In many instances if the *p*K is known then the end point of the titration will be something of the order of 2 units of *p*H, higher or lower as the case may be.

The complete theory of indicators is, however, somewhat complex, but for practical purposes indicators may be defined as substances having one colour in solution at or below a certain characteristic *p*H, a second colour at or above another *p*H value, and an intermediate mixed colour, due to the presence of both the two forms of extreme colour, at *p*H values intermediate between these two. For example, bromcresol purple is yellow at *p*H 5·2 or below, and purple at *p*H 6·8 or above. Between 5·2 and 6·8 the indicator

assumes intermediate tints, any such tint being characteristic of some particular *p*H, and given by a definite ratio of the yellow and purple forms of the indicator.

It should be remarked that this is not true of "one-colour" indicators such as phenol- and thymol-phthalein, which are colourless below *p*H 8·3 and *p*H 9·5 respectively. These indicators show no change of tint, but only an increasing intensity of colour as the *p*H values rise, this intensity depending also on the *amount* of indicator used. With "two-colour" indicators the depth of colour at any *p*H in the effective range depends on the concentration of indicator, but not the tint or shade, which is affected only by the hydrogen ion concentration. Of course, whenever matching is required, both tint and intensity must be alike, and even in ordinary titrations it is best to know how much indicator is present and always to use the same number of drops for a given volume of solution to be titrated.

Every indicator has a characteristic range of about 1·6 units of *p*H, and a large part of the *p*H scale is covered by the different indicators, some of which change in acid, some in more or less "neutral," and others in alkaline solutions. Actually the indicators are either acids or bases, and participate in, or interfere with, the acid-base equilibrium of any solution to which they are added ; it is necessary, therefore, that indicator colours should be very intense and brilliant, so that only a very minute quantity is needed to give a useful colour in solution, thus reducing any interference to a minimum. This can be illustrated by bromcresol purple mentioned above ; 10 drops of a 0·04 per cent solution of this indicator would be ample if used in the titration of 100 c.c. of a colourless solution, and would give a concentration of 0·0002 per cent or 0·2 parts in 100,000, a quantity unlikely to interfere with the *p*H value of any but the most feebly buffered liquids (such as distilled or pure water). Another property required of indicators is that they shall assume their final colour instantly when added to a solution.

It will be seen that the *p*H value at which the end point of any acid-alkali titration is reached depends on the indicator used. This is a very important matter, and since the *p*H value at which an acid or a base is completely converted into its salt depends on its strength or ionisation constant, it will be clear that it is necessary to use the correct indicator for every titration. The titration curve of hydrochloric acid with caustic soda shows that from *p*H 3·5 or 4·0 the curve rises very suddenly, the rise continuing to *p*H 10 or above. Consequently any indicator changing between *p*H 3·5 and, say, 10·0 will change colour very suddenly, as the acid is titrated through the equivalence point. The sudden alteration in colour is what is commonly described as a good "end-point" and is caused by the similarly sudden change in *p*H value ; slow changes in *p*H value mean slow changes in indicator colour and no satisfactory end-point. In this example (hydrochloric acid and sodium hydroxide), as has been long known in laboratory

practice, there is a wide choice of satisfactory indicators; methyl orange, methyl red, bromcresol purple, bromthymol blue, phenolphthalein.

However, a glance at the titration curve of acetic acid shows it to be very different from that of hydrochloric acid. The *p*H value rises slowly from, say, 2·85 to 5·7 or 6, then more rapidly, and then suddenly, for a short distance only, from about 7·5 to 10·5 (the latter figure depending on the concentration of the alkali used) when the alkali added is equivalent to the acid titrated. In this case an indicator changing at 8·0 or above must be used, such as phenolphthalein. Bromphenol blue or methyl orange, which change from 3·0 to 4·6, would slowly pass through all the intermediate colours before the acetic acid was half-neutralised, and would then show the full "alkaline" colour as titration proceeded, and give no indication at all of the "end-point," i.e. the sudden change in *p*H above 7·5. For similar reasons phenolphthalein is useless in titrating ammonia with hydrochloric acid. Here the titration begins at about *p*H 11 or 12 according to the concentration of ammonia, diminishes slowly to about 8 or 7·5, then more rapidly to 6, and finally suddenly for a short distance to 3·5 or 3·0 depending on the concentration of the acid. Clearly an indicator is required which changes between, say, 6 to 5·5 and 3·5 to 3·0. Methyl red, methyl orange, bromphenol blue, and some others are suitable, but *not* phenolphthalein, the red colour of which would begin to weaken before 50 per cent neutralisation, and which would become colourless, after slow changes, at about 90 per cent neutralisation. This explains the old rule for titrations:

Strong acid and strong base — any indicator
Weak acid and strong base — phenolphthalein
Strong acid and weak base — methyl orange.

The theory of titration curves and a knowledge of the change regions of the various indicators enables the correct indicator to be chosen with more precision. It may be added that the old rule does not include *very* weak acids such as boric, or very weak bases. If titration curves for such are drawn, it will be seen at once that no indicator can be suitable since there is no sudden change of *p*H at the equivalence point; nor is there any such rapid *p*H change at the end point if a weak acid is titrated with a weak base, or vice versa. In such cases it is possible to titrate to a specified *p*H only by matching the tint against that given by a known buffer.

The word "neutral" used in association with indicators clearly cannot mean "at or near *p*H 7" except in a few cases. If a solution is described as "neutral to methyl orange" this means that the *p*H lies between 3·0 and 4·6; perhaps in strictness it should mean *p*H 3·7 or 3·8, where the "half-way" colour is given. Similarly with other indicators, although in the case of a one-colour indicator such as phenolphthalein the term "neutral" can hardly be used satisfactorily at all; above 8·3 a pink or red colour is given and

below 8·3 no colour at all ; there is no intermediate tint, only a difference in intensity on proceeding from 8·3 to 10·0.

It will, of course, be realised that this talk skims over the surface of the subject of *p*H value—after all, many large treatises have been written on the matter—but it is hoped that what I have said will indicate some of the pitfalls that await the unwary when they talk too blithely of "*p*H." After all the *p*H value describes one property of a solution, and an aqueous one at that. It does no more than give a measure of the effective acidity (or alkalinity) which may be an important feature, but is seldom of use without qualification.

ERRATA to Vol. VI, No. 2.

Page 142, lines 23, 25 and 28, "W. Navarre" should be "Eddie Navarre".

Page 154, line 19, insert "Dr." between "Schnell" and "E. O.".