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The use of Indicators for Determining the Relative
Strength of Acids. A Class Demonstration Technique.

By

William Hamilton Barrett.

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The use of Indicators for Determining the Relative Strength of Acids; a Class Demonstration Technique.

The fact that the relative strengths of certain acids could be determined by the use of indicators has long been known. One of the first to work up this subject was Salm (1). His work and that of Veley (2) deserves particular mention. However, a later and clearer treatise of this work is given by Clark (3), whose work is followed here more closely than the others. The above papers give most of the preparations and procedure used in this work, therefore their work will not be discussed here but given as a class direction to be followed.

This method, stated in a few words, consists in the comparison of the color given by the unknown acid containing a definite amount of indicator with the color given by the same amount of indicator in an equal volume of some standard buffer solution. The method here used is a relatively simple one consisting only in having a series of standard solutions of varying but known p H values, determined from their method of preparation or by electrometric comparisons.

Meaning of the term p H.

This is merely an arbitrary nomenclature for the hydrogen ion concentration. Thus a 0.1 N solution of HCl (if fully dissociated) is said to have a hydrogen ion concentration of 1×10^{-1} , while a 0.1 N solution of NaOH has $C_H = 1 \times 10^{-14}$. Evidently there may be a steady change in C_H , the neutral point being $C_H = 1 \times 10^{-7}$. Thus a solution might be of $C_H = 6.6 \times 10^{-5}$. As this number is somewhat cumbersome and hard to write a new method was devised, this being called p H. This $p H = \log \frac{1}{C_H}$ gives a much more simple and easier value to handle. Therefore in the above case $p H = \log \frac{1}{6.6 \times 10^{-5}} = \log 1 - \log 0.000066$. $p H = 0.00000 - \bar{5}.81954. = 4.18$. It is readily seen that this is much more easily handled than the other method, yet one is readily converted into the other. It must be remembered however that the higher the p H value the less the hydrogen ion concentration.

Then, to get back to our series of standard solutions, the procedure consists simply of adding to a given amount, usually 10cc of the series of standard solutions a definite amount of the proper indicator, about 5 drops of a 0.04% solution. This

gives a series of shades, each corresponding to a definite pH value. Then 5 drops of the same indicator is put in 10cc of the unknown acid and the series matched with those given by the standards. When a match is found the pH of the solutions is the same. The chief precaution is the selection of the proper indicator.

It has been a long known fact that few indicators have a sharp color change in going over from acid to base but that this change is gradual giving a series of shades as the concentration of the acid is increased or diminished at the turning point. Also, few indicators have the same turning point. Therefore, for a given acid an indicator must be selected which has its turning point at a pH value about the same as that furnished by the dissociation of the acid in question. An indicator whose turning point is above or below the pH furnished by the acid cannot be used. The greater the difference in shades between two pH values which are close, the more valuable the indicator for the range.

The easiest way to select an indicator is to have a chart as given by Clark (3). This consists of a plate on which the transition shades of a number of the important indicators are given as well as the corresponding pH value for each shade. With a chart of this kind much time may be saved as well as the unnecessary waste of the standard solutions.

Standard Solutions.

The standard solutions are prepared by the use of buffer salts, such as citrates, phosphates, carbonates, borates and many others. They absorb H^+ ions by forming a less dissociated acid. Thus in a solution of a highly dissociated acid such as HCl it will be more dissociated the more it is diluted. Then if in this solution there is placed carbonate ions, obviously some of the H^+ ions of the HCl will unite with the carbonate ions to form HCO_3^- which is relatively slightly dissociated. They thus reduce the hydrogen ions in the solution. By regulating the amount of Buffer in this manner the pH value of the solution may be regulated.

The buffer solutions used in this work consisted of a tenth molar solution of sodium citrate, together with a tenth molar solution of HCl, prepared as follows:

Preparation of Standard Solutions.

First calibrate a pair of burettes. If the corrections are small however the calibrations may be discarded. Then the first solution to make up is the acid solutions.

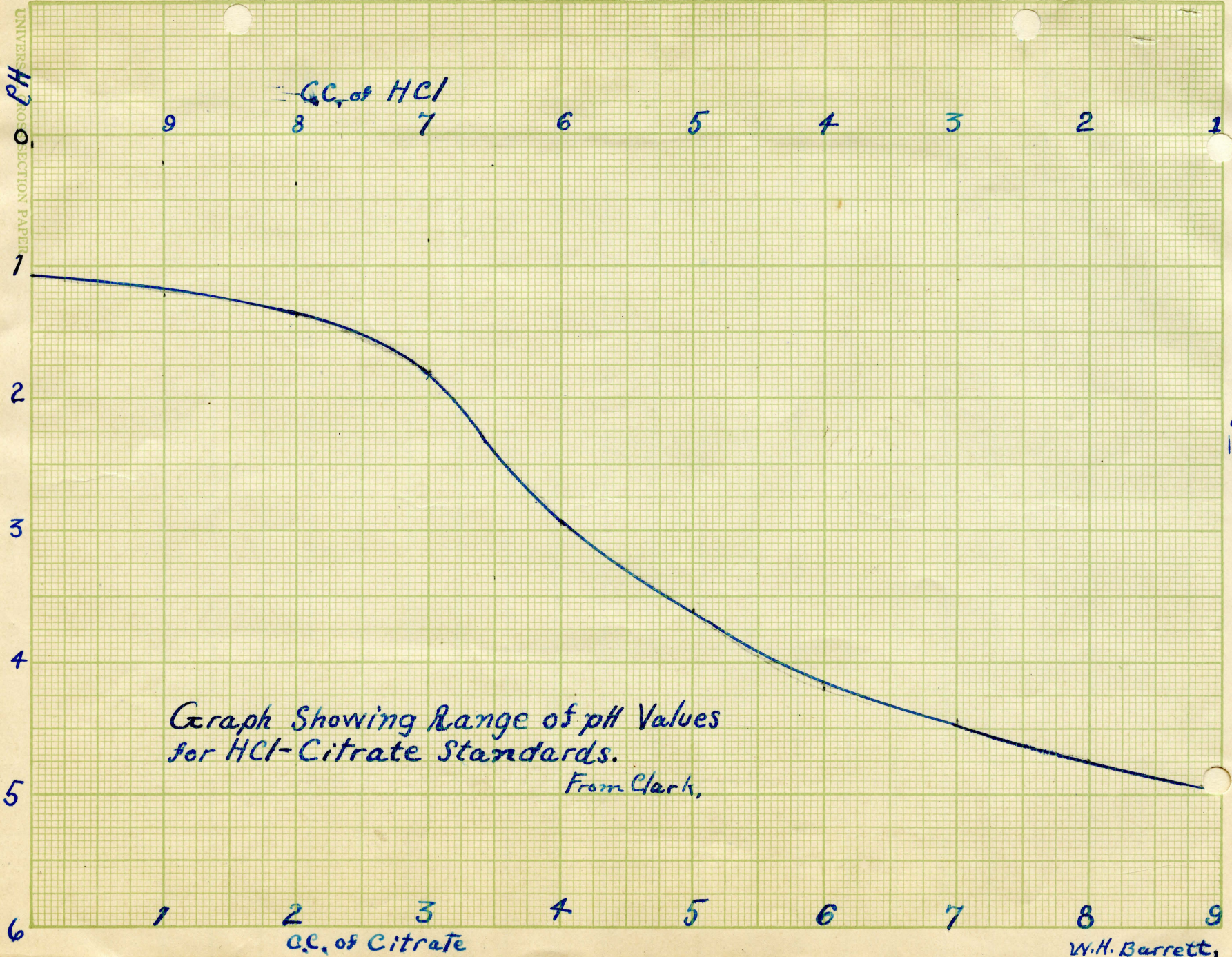
Calculate the amount of concentrated HCl (sp.gr.1.20) required to make up two liters of a 0.1N solution. Make up this solution and let stand for several hours before standardizing, then standardize by titration with a known base or by the gravimetric method. If it is not exactly .1N it should be made so by dilution or adding more acid which ever the case may require but in the latter case the titration must be run over again. However, if this requires too much time the HCl can be used as it is, carrying the factor throughout.

Next calculate the amount by wt. of NaOH required to make up a liter of a 1.0N solution. Add a slight excess (several grams) of this amount as no commercial NaOH is pure. Let this solution stand over night in a pyrex or better still a paraffined bottle and then standardize by titration against the acid prepared above. The utmost care should be used here as we are titrating a 0.1N acid against a 1.0N base and a very small change in NaOH will require considerable acid. When the normality of the NaOH is found it can be used with the factor and not be reduced to exactly 1.0N.

Weigh out carefully 21.008 gms of citric acid. (one-tenth its molecular weight). Dissolve in water and add 200cc of the 1N NaOH then dilute to one liter. This makes a 0.1N solution of sodium citrate.

Then with the 0.1N acid solution and a 0.1N sodium citrate solution we are ready to make up the series of standard solutions, the sodium citrate being used in this case as the buffer.

Select 28 flasks capable of holding 100cc each, these should be preferably pyrex, glass stoppered, and graduated for 100cc. To the first add from a burette 90cc of the .1N HCl, to the second 80cc, to the third 70cc, etc. Then as the curve here becomes much steeper, (shown in accompanying diagram), solutions should be made up for smaller variations of the acid. Between 70cc acid and 50cc acid make up a solution for every change in 2cc. Thus add to the series 68cc, 66cc, 64cc, etc.-----50cc HCl. To the next bottle after this series add 45cc HCl and then 40cc HCl. For the rest of the curve vary the strength by 10cc portions, thus 30cc, 20cc, 10cc. Then



30

6

make up each of the above to 100cc by adding from a burette the required amount of sodium citrate solution. If the bottles are graduated this may be done by simply diluting with the .1N sodium citrate up to the graduation. If these solutions are kept in a pyrex glass stoppered bottle they may be kept for sometime without an appreciable loss due to the solution of the glass. The bottles should be labeled with their pH value as taken from the curve.

The above solutions give a range in pH from about 1 to 5. Above and below these values the slope of the curve becomes so small as to be impracticable for use. For greater or less values of pH other buffers may be used. See Clark.

For the above series the following indicators were found to be the most desirable.

Indicator	pH range.
T.B.- Thymol Blue (acid	1.2 to 2.6
E - Ethyl Orange	2.6 to 3.4
B.P.B.- Brom Phenyl Blue	3.4 to 4.6
M.R.Methyl Red	4.4 to 5
M.-Methyl Orange	2.5 to 3.1

If these indicators are not in solution in the laboratory make up a 0.04% solution of each and keep them in a well stoppered bottle.

Acids under Examination.

The acids should be recrystallized even though it is a C.P. acid. A commercial acid should be crystallized several times.

Saturate a hot solution of the acid and filter while hot through a fluted filter paper in a hot water funnel. If the solution is colored boil with animal charcoal before filtering. Set the filtrate aside to crystallize. When it is thoroughly cool filter using suction and dry in the air.

When thoroughly dry make up a .01N solution of the acid by dissolving one hundredth of its molecular weight, (if it is a monobasic acid) in a liter of water. Let the solution sit for several hours before making the tests.

Choice of Indicator.

Take 10cc portions into several test tubes and add to each 5 drops of a different indicator whose working range is supposed to be near the pH value of the acid. Compare these colors with the shades given by a color chart prepared as the one given by Clark. If the color of the solution with a certain indicator comes within the range of shades for that indicator it may be used in the comparisons. If such a chart cannot be obtained the colors given by certain indicators within their active range may be so memorized by working with the standard solutions that these preliminary tests may be carried on satisfactorily.

Comparisons.

Select the range of standard solutions corresponding to the effective range of the indicator determined as above, and pour 10cc of each solution into a series of test tubes arranged in order. The pH value increasing in regular order through this range. Into each test tube place 5 drops of the indicator and shake. This should give a series of shades of increasing brightness of color.

To 10cc of the acid solution in another test tube add 5 drops of the same indicator as was used in the standard solutions. A color will result which matches some where along the scale of standards. Match this color by comparison as nearly as possible. When a match is obtained the pH values of the solutions is the same.

If the change in color between two adjacent solutions is slight they are best compared by use of a comparator made as follows:

Bore two holes about an inch and a half apart into block of wood. The size of these holes being just large enough for the test tubes to fit into them. Then about an inch from the bottom of the block bore a smaller hole at right angles through each of the other holes. These are for the purpose of looking at the test tubes when placed in the upright holes. The entire block should then be painted black. With such an apparatus very accurate comparisons can be made.

If the solutions of the acids are colored or murky they should be handled as follows:

Bore two more holes for the test tubes back of those already in the block and also intersecting the holes for observation.

Then in the front hole of one pair, place the standard solution with indicator and back of it a test tube full of the acid but with no indicator. In the other front hole place the tube of acid with indicator to be tested and back of it a tube of clear water. Then make the comparisons as above.

In this manner the same thickness of solution and same amount of color is looked through in both sides and thus eliminates almost entirely any error due to the coloration of the solution.

The above method although an approximation gives some very close results, which in many cases may be all that is required and this method is very saving both in time and expense to some other more exact methods.

The potentiometer method is another more exact method but requires more equipment and the methods of manipulation are not as simple as the one given. Therefore the colorimetric method of determining the pH value is coming more and more into use especially in commercial laboratories where the approximate pH of a solution is required and a quick method of finding it is desired.

Several organic acids were run through the above procedure and their pH value found. In each case a 0.01 N solution was used and found to be the most satisfactory. In some cases however the acid may not be soluble to this extent and a more dilute solution would have to be used while in other cases the acid may not lend itself at all to this method on account of instability or insolubility. In this work Cinnamic acid was tried and found not to give very satisfactory results.

For each of the acids used the hydrogen ion concentration of each of the acids was calculated as a check and in each case no error was found greater than would be expected from the nature of the work.

There were two methods used to calculate the pH value from the data given:

(1) The first method is based upon the law that $\frac{C_H \times C_A}{C_{HA}} = K$. This K being given in the tables.

Thus from Scudder (5). At 25 for benzoic acid $K = 6.6 \times 10^{-5}$
Then for a 0.01N solution which is X dissociated

$$\frac{x \cdot x}{.01 - x} = 6.6 \times 10^{-5} = .000066$$

$$\frac{x^2}{0.01 - x} = 0.000066$$

$$\bar{x} = 0.00078 = 7.8 \times 10^{-4}$$

$$P H = 3.12$$

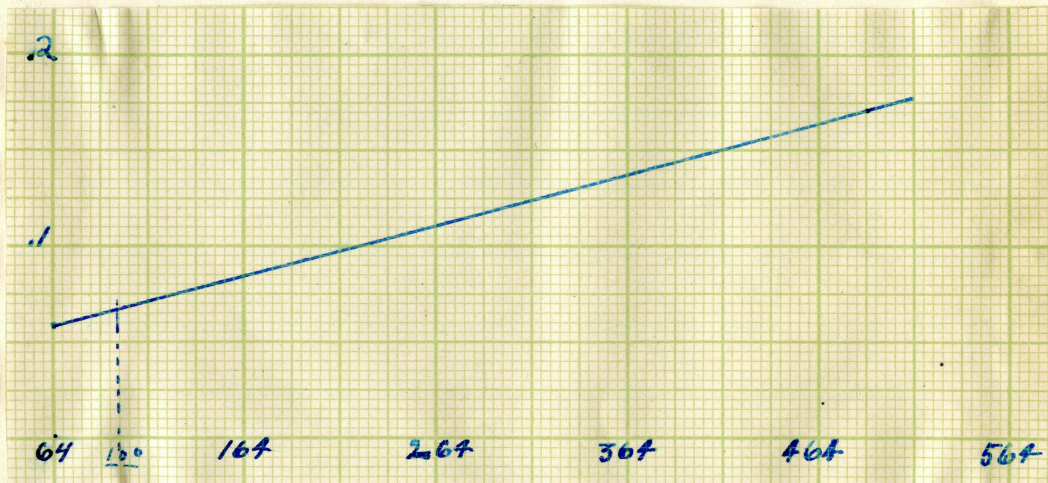
(2) The next method is based upon the equivalent conductivities at varying dilutions. Thus Scudder gives at 25 for a $\frac{1}{64}$ mol. the conductivity is 22.3. For $\frac{1}{512}$ mol. conductivity is 59.8. For infinite dilution the conductivity is 351.

Then the conductivity at any dilution divided by the conductivity at infinite dilution gives the percent dissociation. Thus $\frac{\Lambda_r}{\Lambda_\infty}$ = degree of dissociation:

$$\text{Therefore at } \frac{1}{64} \text{ mol. } \frac{22.3}{351} = 0.0635$$

$$\text{At } \frac{1}{512} \text{ mol. } \frac{59.8}{351} = 0.1703$$

Plot these values as ordinates using the volume as abscissas. The curve is near enough a straight line to be so regarded.



Then take the value from this curve for $\frac{1}{100}$ we see that it is about 0.0655% dissociated.

$$0.0655 \times 0.01 = 0.000655 = 6.55 \times 10^{-4}$$

$$P H = 3.18$$

Each of the acids used was calculated by these methods and the mean results taken for pH.

The following table gives the acids used with the result obtained as well as the calculated pH.

Acid $\left(\frac{M}{100} \right)$	Indicator	Result Calculated.
Sulfanilic	M	pH= 2.35 - 2.60
Benzoic	M	pH= 3.1 - 3.12
o-Hydroxy-Benzonic	M	pH= 2.8 - 2.55
m-Hydroxy Benzonic	B.P.B.	pH= 3.1 - 3.36
p-Hydroxy Benzonic	B.P.B.	pH= 3.15 - 3.3
o-Amino Benzonic	B.P.B.	pH= 3.3 - 3.6
m-Amino Benzonic	B.P.B.	pH= 3.75 - 3.45
p-Amino Benzonic	B.P.B.	pH= 3.45 - 3.55
m-Nitro Benzonic	M	pH= 2.60 - 2.78

In no case is the calculated pH much different from the experimental value of pH than would be expected from the method of determination.

The student will find that by following the above procedure some very accurate and interesting results may be obtained. This method gives a clearer understanding of what is really meant by the strength of acids as expressed by their hydrogen ion concentration, yet it is simple enough to be carried on by any one who knows only the first fundamentals of chemistry.

By this comparison the relative strengths of many acids become much clearer understood. It does not give a lot of facts to be memorized such as tables and so forth, but has also an appeal to the eye in that hardly any two acids give the same color exactly. Nor is the field limited to the acids used, in fact it is almost unlimited any weak acid and especially the organic acids may be tested by this method, although in some cases the result does not appear to correspond with that obtained by other methods, yet it gives a very fair estimate. Nor is the field limited to acids, as such, alone but the hydrogen ion concentration of other solutions and mixtures may be determined in this manner, such as the blood, gastric juice, and many other secretions of the body, where a hasty determination is required.